THE CEMENTATION
OF
IRON AND STEEL

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THE CEMENTATION OF IRON AND STEEL

BY

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TRANSLATED FROM THE ITALIAN

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PREFACE

The cementation of iron or steel is perhaps, of all metallurgical processes, that which to-day is still applied industrially with the greatest empiricism, and it may be asserted that what the English so effectively denote by the expression "rule of thumb" is the only rule followed in the greater part of cementation establishments.

Now, while this might have been justified, a few years back, by the lack of precise scientific data on the process of the carburization of iron or steel, this is no longer so, since numerous investigations which have been carried out have furnished abundantly the information necessary to carry out any cementation under the simplest and most easily controlled conditions, with less expensive materials, and in such a way as to obtain, certainly and logically, exactly predetermined results. It would therefore be desirable, since it is now possible and even easy, that cementation establishments should begin to use only cements whose composition and manner of acting are known exactly, and that the persons who direct them should realize that it is very easy to prepare for themselves cements which are much more simple, efficacious and certain—and, above all, by far much less expensive—than those which they now buy at very high prices without knowing even approximately what is concealed under the mysterious names which dealers in cement powders usually give to their humble products.

I believe that such an evolution can and must soon come to pass as, for example, that which has almost completely stopped the very lucrative trade in those mysterious powders which, thrown in small quantities into the molten steel, before casting, were supposed to relieve the steel founder of all his ills.

It has seemed to me that, to facilitate such an evolution (at least in small part) I could usefully contribute a résumé of the results to which the scientific investigations carried out on the process of the cementation have led.

Of the criteria which I have thought fit to observe in the compilation of such a résumé I will say here, to prevent any one from seeking in this volume that which I have not thought I could include, that it is neither an organic or systematic treatise on the physico-chemical theory on which the study of cementation may be based nor a recipe book intended to reveal the secrets of the dealers in cement powders.

In the first part of this volume I have tried to summarize the results of the scientific investigations carried out up to the present on the process of the cementation.

Many of the fundamental questions—especially theoretical—regarding cementation have not yet been completely, certainly, and definitely solved so that, for a useful practical application of the researches carried out up to the present, a few synthetic rules are not enough, but we must also take into account a large number of data which are insufficient (because they are not sufficiently coordinated experimentally) to constitute complete and organic theories.[1] It follows that, lacking the possibility of collecting systematically the data thus far acquired so as to establish well-defined theories, and it being necessary, on the other hand, to summarize *all* these data, the chronological order had to be followed in this first part of the treatise.

I have thought it well, however, to show—in the fifth chapter of the first part—how the data collected in the first chapters, besides constituting a most useful basis for the rational technical application of the processes studied, can even now be gathered logically into groups in such a way that, without being adequate to furnish the material for satisfactory theories, sufficient conclusions can be drawn from them to clear up many of the more important theoretical questions and to point out clearly the surest and shortest way for further studies and researches.

In this first part I have tried to collect all the data at present at our disposal for the rational technical application of the processes of cementation, data which should already be amply sufficient to emancipate workers in this art from the purchase of cementation powders of unknown composition.

The necessity of avoiding long digressions has constrained me to presuppose in the reader a sufficient knowledge of metallography and metallurgical chemistry.

In the second part of the volume I have tried to bring together some examples of the means to which recourse may be had to realize in practice the conditions which the data in the first part indicate as being best suited, in any given case, to obtain a predetermined result, and of the means for controlling the results obtained.

I repeat, however, that the rules for carrying out the cementation proper in such a way as to obtain given results are those contained in the first part of the volume.

In the choice of examples of apparatus and of technical processes cited in the second part, I have tried to limit myself, as far as possible, to those forms of apparatus and to those processes which I have had occasion to use and study personally.

---

[1] Among the many examples which might be cited to prove the justice of this assertion, I will mention only the aggregate of experimental data relating to the phenomena of oxidation which under certain definite conditions accompany the carburizing action exercised by carbon monoxide on chrome steels and the rules which enable us to establish the conditions under which such phenomena do not take place. I will mention also the aggregate of the data on which are founded the rules for obtaining predetermined concentrations of carbon in the cemented zones, working with mixtures of carbon monoxide and hydrocarbons.

TRANSLATOR'S PREFACE

When Dr. Giolitti's work appeared in Italian, in 1912, it was clear to metallurgists that this was an epoch-making contribution to the literature of iron and steel. For several years the scientific papers on cementation coming from Prof. Giolitti's laboratory have been numerous and important, and his industry and brilliant investigations have practically cast new light upon the whole subject. While regretting that the author's commercial connections prevent him telling all he knows on several important questions, such as the carburization of armor plate, yet he has nevertheless made the industrial and scientific worlds his debtors by the vast amount of detailed information he has given with regard to the scientific investigation and control of cementation processes.

Regarding the translation, it may be remarked that the Italian language is much less direct than English, and that a nearly literal translation would have made tedious reading. Without entirely deviating from the form of the original, we have striven to render the sense and the ideas in the nearest acceptable English form. Professor Richards is responsible for the metallurgical accuracy of the translation, while Dr. Rouillier shouldered the bulk of the task of rendering the original into English.

LEHIGH UNIVERSITY AND
JOHNS HOPKINS UNIVERSITY.
May 22, 1914.

JOSEPH W. RICHARDS.
A. ROUILLIER.

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INTRODUCTION

By the name "process of cementation" is meant mits of partially or totally carburizing an iron or steel ing it to fusion, and in such a way that the carburize preserve the structure and the properties of a true st tained by heating the object to a high temperature- point—keeping its surface in intimate contact with ca which decompose at the temperature worked with, the majority of cases the carburizing substances—or " manufacture of cement steel are solid; such, for exam lamp-black, various organic substances, etc. Soli employed in the form of powders in which are imm cemented; in such a case it is necessary to secure inti ment over the whole surface of the metallic piece.

Besides the solid cements, liquid cements (for exa cyanide) and, still more, gaseous cements (such as the carbon monoxide, etc.) have found wide applicatio times. Both offer in many cases very marked advan solid cements; not least among such advantages is th of the carburizing substance with the whole surface complete uniformity of carburization at every point of are also often cases where the simultaneous use of sol cements is advantageous.

In all cases the process of cementation consist tration of the carbon yielded by the cement i

The first indications of a process for the transfor
steel which presents the characteristics of a true proc
found in the work of the Sienese metallurgist Vann
lished in 1540 under the title of *Pirotechnia*, and in the
by George Agricola, published in 1556.

The process minutely described by Biringuccio a
in heating for a long time the billets of soft iron in
latter yields up carbon to the soft iron, behavin
"cement."

Beck, in his classical *Geschichte des Eisens*,[1] after
tion of this process which is given by Agricola, adds t
lished with certainty whether in the Middle Ages or i
of cementation was known analogous to that which h
cation in recent centuries and is even to-day the m
that is, the partial transformation into steel of iron
obtained by heating these objects in contact with
protected from contact with the air. Beck considers
facturers of daggers, arms, needles, etc., knew such pro
times but kept them secret, transmitting them verb
Such a hypothesis seems confirmed by some legend
found at the beginning of the Middle Ages.

In the sixteenth century there were certainly know
tion proper, based on the use of carburizing powder
of carbon mixed with organic substances. Such pr
exclusively with the object of obtaining a superficial
of being hardened by quenching—in the iron objects
after being finished, to the process of cementation.
to-day also the process of cementation is widely empl
gous purposes; in this case the process is frequently c
of "case hardening" (Italian *tempra a pacchetto*, C
French *trempe à paquet*).

at the beginning of the seventeenth century in
and during the same century it spread into the ot
cially to Belgium and Germany.

Up to this time (end of the seventeenth centur
tion, like all other siderurgical processes, continu
to exclusively empirical data which alone had le
later to its improvement, and the first attempts to
by means of systematic investigations, the real cou
tation date only from the beginning of the eighte
both in point of date and in importance—of the
the above object we owe to the French scientist
with great success, the scientific study of the m
problems.

The investigations of Réaumur on the cementa
of a series of Memoirs presented by the author befo
of Paris during the years 1720–1722, forming the
titled: *L'art de convertir le fer forgé en acier et l'art*
faire des ouvrages de fer fondu aussi finis que de fer
title, the second part of this work—which has si
prises a series of investigations on the manufactu

As in the preceding centuries, so also at the
century, the processes of cementation proper, w
in Germany, in Italy and in England, for the pr
subsequently worked, were jealously kept secret
turers, each one of whom boasted the superiority
France crude cement steel was not then manufact
of *case hardening* for producing, as we have seen
forged iron objects a thin layer of hard steel capa
known and applied. Réaumur, starting from t
these latter processes must be entirely analogous t

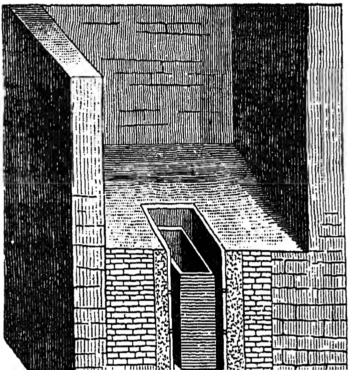
to transform iron into steel, Réaumur studied s
the various materials then used in France for
each one alone or making mixtures of them.

On the basis of results from a large number
studied the action of a multitude of substances (
plants, many salts, fats, vegetable and anima
reached the conclusion that the best effects wer
mixtures with powdered wood charcoal as a bas
and other substances. An example of the mixtu
mur for the manufacture of cement steel is the f

Powdered wood charcoal..............
Ashes.......................
Lamp-black....................
Salt.........................

Réaumur gives many examples of such mixt
be followed in varying their composition accordi
which it is desired to transform into steel and
the product
tain, qualiti
and classifies
the raw mat
on the basis
surface of fra

Réaumur
very great im
of heating, a
and precise r
and the pla
by him, in o
ditions of the



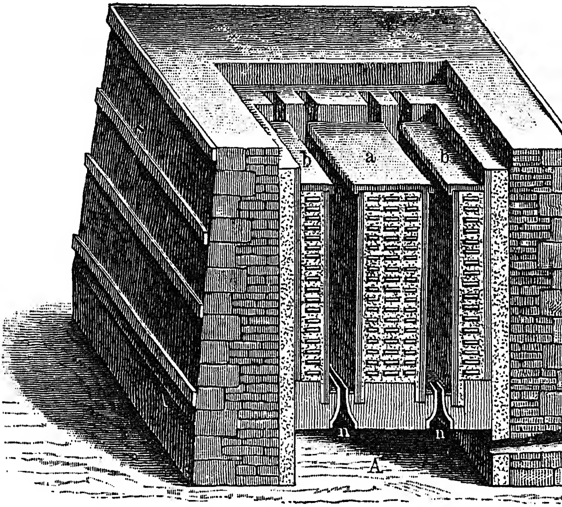
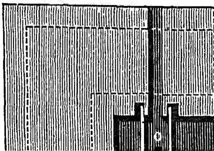


FIG. 2.

steel *increases in weight*, so that (there being no valid r *a priori* that steel is a *purer* material than iron) the hypot accepted that the transformation of iron into steel consists of the former can no longer be considered exact, and it is n that the effects of cementation are due, not to the elimina of substances which rendered it impure, but to the pen foreign substances which evidently must be contained in the powders used as *cement*. Now, given the theory still prevalent at the beginning of the eighteenth century concerning the constitution of the sub-



the choice of the cementing mixtures, of the raw mate
treatment best adapted for obtaining good result
proper, so for case hardening, the *cements* recomme
fantastical mixtures of organic substances, such as
and urine of certain animals. But we have no righ
at this when we consider the fact that many of the
still largely used to-day and placed on the market un
and under curious contracts of secrecy, are no less
Réaumur; nor do they give better results.

The investigations of Réaumur gave a very strong
of the manufacture of cement steel, but, contrary to
other nations profited more widely by them than Fra
did not produce iron of a quality adapted to furnishin
of cementation.

Within a few years after the publication of the inve
many factories of cement steel sprang up in various
while the French factories had very little success (for
mentioned), those established in Sweden (for exam
opened in 1725), in Germany and in England flourish

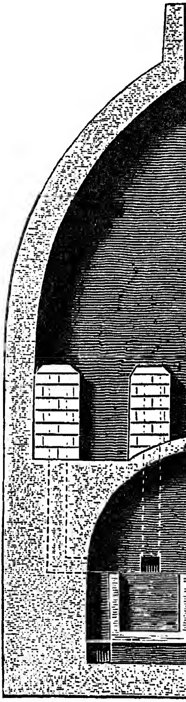
In the latter country it appears that the manufact
imported in the year 1710 by a certain Bertram, a Ger
learned the secret in his native country. But, as in
in England, this manufacture began to develop exte
labors of Réaumur had placed at the disposal of man
execution which were much more precise and effica
jealously guarded from the first by a few manufactu
from the latter the monopoly of an industry which at
large profits. Newcastle and Sheffield became the p
manufacture of cement steel in England; here the ma
out in furnaces of the type of those shown in Figs. 4,
same principle as those proposed by Réaumur and n

blisters which characterize the surface of the bars of cer
to-day in England to designate this product, as also th

The superiority of cement steel manufactured in Er
tially to the superlative quality of the iron used as r
which the English manufacturers procured almost e
purchasing the entire production of some of the best Sw
was very natural, therefore, that another result of this
and the development of the industry of cement steel in Sweden. The industry, however, did not attain either in Sweden or in Norway (where, also, it began to develop at that time) the state of perfection reached in England.

In America also, after a period of unsuccessful attempts, the manufacture of cement steel began to develop in the second half of the eighteenth century, but it did not attain marked importance until the beginning of the nineteenth.

The manufacture of cement steel reached a still greater development in England when an English clock-maker, Benjamin Huntsman, discovered in 1740 and afterward made practically workable on a large scale the crucible process of melting steel. After many unsuccessful attempts the difficulties



Very soon, however, the introduction of new met
of steel, capable of furnishing a product of good
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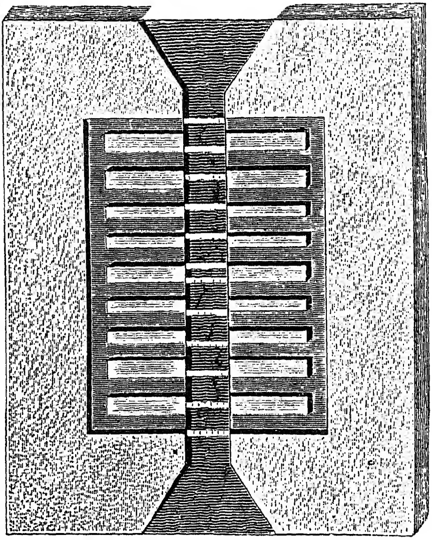
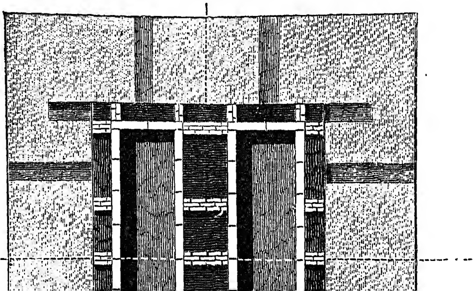


FIG. 5.



steels manufactured by the new processes, it neverthele great superiority in *quality*, so that its new uses, necessar cases in which the high quality of the material is conside have constrained manufacturers to study the process of ce obtain by it the best product at the least cost. On the ot improvement in mechanisms, placing at every moment l of the metal used in them the problem of obtaining in parts the maximum superficial hardness combined with n brittleness, resulted in causing the process of surface cem objects of soft steel to assume great importance, especially by the name of *case hardening*, which, as we have seen, and applied at the end of the sixteenth century.

A consequence of the facts just mentioned is the recent since the close of the nineteenth century, made both in th and technical applications of the process of cementation, at on a large scale and according to precise and delicate rules, burization of machine parts made either of carbon st types of those special steels which have found such wo in mechanisms.

We shall study further on the most recent processes the chemical theories on which they are based, and limi noting briefly the historical development of each up to the teenth century.

As we have already seen, the theoretical conclusions d on the basis of his numerous and painstaking experiments r of the process of cementation, contained, together with a la true, grave errors, which, however, were the inevitable ical theories universally accepted at the beginning of the

But very soon, more precisely in the second half century, the Swedish chemist Bergman began by show

Réaumur, of Bergman and of Scheele and interpre the new theories, were easily able to show that the when combined with pure iron in various proporti to cast iron, was none other than the element ca made use precisely of the phenomenon, already obs increase in weight of iron when it is transformec cementation in the presence of wood charcoal al contact with air and moisture, thus showing that s be due only to the gradual *absorption* of the carbor

The investigations of Vandermonde, Berthollet with equal clearness many of the most importan were followed by a large number of analogous resea scientists, all on the basis of the new chemical theo opment of the latter, at the end of the eighteenth a nineteenth century, brought about the result that v of siderurgical processes could be clearly interpret basis of sure analytical data. All these investigati basis of that scientific study of iron which Jüptne the fact that the process of cementation consists sir sion of the carbon into the mass of the iron.

After the establishment of this fundamental fa reinstatement of cement steel, from the point of viev tion, in the same category to which belong steels obt the history of the development of the theoretical k nature, the properties and the intimate structure c forms a special chapter in the history of siderology, b theory concerning steel, knowledge which it woulc opportune to discuss here and which I must assume

It is quite proper, therefore, to say that, sin Vandermonde, Berthollet and Monge, the task of

disorderly, discordant and often unfounded individual
see this better later on; I mention the fact now only b
explain the absolute empiricism which thus far has
dominates the industrial application of the processes of ce
too, while the technology of almost all other siderurgica
gaining new scientific data from the systematic and ri
chemical phenomena on which those processes are based

We have already seen that the mixtures, in general qu
mended by Réaumur as "cements" were quickly aba
manufacturers who, while largely taking advantage of
by the French scientist for the construction of his furna
of the heating and, in general, the conduct of the various
as cement simple powdered wood charcoal. The exampl
very quickly followed by manufacturers in other countri

Nevertheless, even though the researches of Vanderm
Monge had confirmed the reasonableness of the Englis
as we have already seen, that the process of cementation
sion of *carbon alone* into the iron, yet the opinion contin
the addition of suitable foreign substances to the wood c
of more complex carburizing substances it was possible t
time necessary for a given amount of cementation.

Such an opinion, which, as we shall see further on, h
been confirmed scientifically within the last few years,
whole of the nineteenth century to an immense number o
the known processes of cementation, attempts which had
ject the discovery of the substances or mixtures most effic
which were (and in part still are) conducted along exclusi

The first one who tried to use cements essentially
proposed by Réaumur was Prof. Vismara of Padua, who
the nineteenth century showed that excellent cement stee

and gaseous), the compounds of cyanogen occupy o places, but we shall see that their real efficiency is generally attributed to them. Thus Caron, in propo ess of cementation (still widely in use to-day) based mixtures of wood charcoal and barium carbonate, of the latter substance to its tendency to form, with cyanogen compounds. In reality (as we shall see l barium carbonate is, in this process, quite different f by the theory of Caron, a theory which, however, is by many "experts," and referred to as correct in m

Some success was obtained in the United States by a process of "liquid cementation" based, like th and by Biringuccio, to which I have called attenti cast iron as cement. This process, however, did no

Meanwhile, for reasons which we have already se of cement steel proper, intended to be subsequently ing, the importance of the industry of partial cementa of finished mechanical pieces was constantly incr to what is needed in the manufacture of steel intend it is merely a question of obtaining maximum ca time, the application of the process to the partial pieces intended to furnish products which, without and solely as the result of cementation and tempe mechanical properties certain given conditions often presents a large number of complex problems, the so precise knowledge of the methods of treatment best a given raw material, a product having exactly the

The complexity of such problems, which we shal the active researches and the innumerable attempts of the nineteenth century to perfect the *technique* of cementation of finished pieces, processes which ext

PART FIRST

THE CHEMISTRY OF CEMEN
PROCESSES

CHAPTER I

THE FIRST SCIENTIFIC INVESTIGATIONS ON THE CEME

We have already seen that the theoretical conclusions ning of the eighteenth century by Réaumur concerning t the chemical composition of the iron undergoes during the tion were, although based on scrupulously exact experim totally erroneous, on account of the erroneous hypothese all, of the nature and chemical composition of the materi seemed to indicate as being the most efficient for the tra into steel. The only fact established with certainty by fully confirmed, is the increase in weight of the iron whe into steel by means of the process of cementation, a f interpreted as proof that the iron, in passing into steel, *abs* But we have also seen that the true nature of the substan with iron, transforms it into steel, was identified only si by Vandermonde, Berthollet and Monge, who, in 1786, basis of the new chemical theories of Lavoisier the results carried out a few years before by the Swedish chemists B were able to establish with certainty that steel differs from because it contains a greater quantity of carbon, and cementation is nothing but a process of diffusion of the c into the mass of the iron.

The views of the three French scientists on the natu cementation, like the other theories formulated by the other siderurgical processes, were repeatedly confirme

in a memoir published in 1841 in the *Annales des M*
the carburizing action of wood charcoal, then gene
material, by assuming that the oxygen of the air wh
of the wood charcoal contained in the cementati
carbon itself, forming first carbon dioxide and the
carbon monoxide would then yield to the iron half o
over into carbon dioxide, and this would again b
carbon monoxide by the action of the carbon used
the cycle of reactions would be reproduced inde
monoxide would act as a *carrier* causing the pene
the solid metal.

We shall see later how the hypothesis of Leplay
within very recent times. It was not, however, t
Gay-Lussac, in a memoir published in 1846 in the
Physique, raised many objections not only to the hyp
to the later one of Laurent, according to whom it i
its vapor, formed at high temperatures, which
during the process of cementation. Gay-Lussac c
reason for excluding the possibility that the carbon
dissolving directly in the iron without the interve
and that many other facts prove that all substanc
with each other when brought into contact, whate
aggregation, even though the solid state must, to b
least favorable for the operation of phenomena d
affinity.

The objections raised by Gay-Lussac against t
and of Laurent opened the discussion, which has
present day, concerning the part played by gases i
tion. And we shall see later how it is precisely wit
related the greater part of the experimental researc
last fifty years on the cementation process, resea

Thus Caron, in a series of memoirs published from 1 *Comptes Rendus de l'Académie des Sciences*, thought that h establish, on the basis of many experiments, that the pr cementation is always due *exclusively* to the action of volati confirming and partly extending the theory formulated in according to whom cyanogen and cyanides have a most i in industrial cementation, in which they act as " carriers surface of the iron subjected to cementation.

Since the researches of Caron, and still more the polen gave rise, may be considered as the starting point of scien process of cementation, it seems well to give here a brief contents. More detailed abstracts of the scientific wo especially of his investigations on cementation, can be foun article by Captain P. Nicolardot, published in the *Revu* although it must be said that this article attributes, in gen too unqualified value to the evidential value of Caron's ex

In his first memoir on cementation (1860), Caron ass pound which gives rise to the carburization of the iron than a volatile cyanide, capable of penetrating into the dilated by heat. He believed that he proved his asserti of the fact that, by heating in a porcelain tube bars of ir carbon in small pieces and making a current of dry gaseous through the apparatus, there is obtained in two hours a mm. thick; while, on the other hand, if all the other ditions are kept constant, and some other gas (such as monoxide, nitrogen, air, etc.) is made to circulate in cementation whatsoever is obtained. From this experin first of all that none of the gases which are ordinarily prese reactions is capable of cementing iron, and he includes i *inert* gases hydrogen, carbon monoxide, nitrogen, air, e formed ammonium cyanide which alone yielded transforming it into steel, so that the volatile cyan agent of the cementation. This opinion he believ when, in later experiments, he was able to prove even when alone, behaves like an active cement, becomes considerably more rapid when the carbon nated with an alkali or with an alkaline earth an made to circulate in the apparatus used for the facts possess so much the greater value for the hyp claims to be able to establish that the only alkalis are effective (in the sense just indicated) are those investigations of his) can form, under the conditio ments on cementation, volatile cyanides. Thus baryta had been found effective, lime, on the ot entirely inert.

In the meantime, the Englishman Saunderson series of investigations from which he drew the c iron it is *necessary* to have recourse to the simult (for example, in the form of ammonia) and of ca form of ethylene), while cementation could not b *pure and isolated* carbon, carbon monoxide, ammoni (1861), observing that under the experimental cond ammonium cyanide must be formed, drew from th technologist a new confirmation of his hypothesis.

As the result of his experiments and his hypothe the use of a cement (still employed to-day) consis parts of carbon with one part of barium carbonate ciency of which, inexhaustible by use, he attribute tion of barium cyanide. This is very slightly v escape from the cementation boxes, and is formed of the carbon and of the nitrogen of the air occl

cemented zones obtained with them. Thus he draws att
that ammonium cyanide is, of the various cyanides, the on
as cement, shows in the most marked degree the inconv
excessively carburizing the iron, transforming it quite ea
instead of steel, while this fact does not manifest itself wh
is used. This is because ammonium cyanide is, of all the
one which is the most easily decomposed.

But if Caron was able to feel sure that in the processes c
the sole agent of the carburization of iron is cyanogen with
had to abandon his theory in some special cases, being com
for example, that in the cementations obtained by mean
it is not possible to assume the intervention of cyanide
however, that the hydrocarbons used as cements, on accou
decomposability, always carburize the iron too much, tr
cast iron instead of steel. Therefore the *only* compounds
ing in practice a true cementation proper (or a transforr
steel) are the alkali cyanides, which he considers as "the
carbon which are undecomposable and volatile."

Meanwhile Frémy, in a series of memoirs also publish
Rendus de l'Académie des Sciences, believed that he had be
by means of a large number of observations that the impo
tion of nitrogen in the process of cementation was by far st
attributed to it by Caron. In fact, he believed that he
results of the earlier researches of Faraday, Schafhäutl ar
had revealed the presence of nitrogen in steel and in ca
show[1] that nitrogen is, together with carbon, a *necessary* c
so that "on peut dire qu'on acière du fer en l'*azotant* en pr
et qu'on le *désacière* en le *désazotant* par l'hydrogène." ("
iron is made steel by absorbing nitrogen in presence o
steel is changed to iron by removing its nitrogen by hydro

tists, as is evident from the animated discussio the Academy of Sciences, the communications c

But very soon the investigations which Carc the same time as Frémy, led him to results whic to harmonize with the theory of Frémy, whence a the two scientists. The discussion ended with Frémy's theory, but the cementation experim made by Caron to demonstrate the lack of f theory constrained their author himself to mod his original theory and to admit that certain vo (as, for example, various hydrocarbons) can ce intervention of nitrogen.

Three years later (July, 1864) a new scientif by Margueritte concerning the results of Caron' in the meantime, although continuing his intere tion of steel, on the nature of the process of tem further experimental studies on cementation, c of his Memoirs of 1864) that the question was basis established by him.

Not convinced of the exactness of the hyp began an experimental study of the process c the results obtained in a series of communicatio emy of Sciences of Paris, beginning in July, 186 Margueritte bases his thesis, contrary to the hy possibility of *direct* cementation by means of ca tact, and of the possibility of cementing iron by ide, merit brief mention, for many of the discu place on the same argument spring from these e out in opposition by Caron.

In his first communication[1] Margueritte de place the air from the apparatus. This done, he rapidly r ture of the tube to bright redness and kept it so for son without interrupting the current of hydrogen, let the ap moving the boat from the tube, the experimenter was ab diamond had perforated the sheet of iron and had fallen gether with a small globule of cast iron. After having experiment with diamonds and sheets of iron of various dim always obtained the same results, Margueritte heated in t and under identical conditions (always in a current of hyd 1 1/2 mm. in diameter, immersed for half of its lengt in a platinum boat; the experiment being finished, he cou the part of the wire which had been in contact with the cemented while the other part was not and remained insen Analogous, but still more conclusive results were furnish periment in which graphite or sugar carbon, first ignited a current of hydrogen, was substituted for the diamond c

Margueritte justly observes that if the hydrogen used had reacted with the carbon to form acetylene or any ot carbon to which might be attributed the cementing action wire ought to have been cemented along its whole length was not the case, Margueritte considers it as proved that passing into steel or cast iron, when it is heated in contac that the transformation of iron into steel takes place even vention of nitrogen.

In a second note[1] Margueritte describes a series of e out by heating pure iron in a porcelain tube glazed insid which he circulated a current of very pure carbon monoxi

His experiments, executed with minute care, led him trary to what Laurent and Leplay, and more recently C that pure carbon monoxide markedly cements iron.

In his new experiments Margueritte found a f
hypothesis of Frémy on the function of nitrogen in th

To the two notes just cited Margueritte added
basis of the data from his own researches and thos
he formulates his theory of cementation in the
combines with carbon and is transformed into steel b
and also by the decomposition of a carburetted
carburization are present and act simultaneously in

I shall have occasion later to again refer to the c

Margueritte ends his third Memoir by explicitl
experiments constitute a new demonstration of t
Frémy's theory and summarizes his views on the
them from his investigations on cementation, in a f
being quoted in full as epitomizing, in advance,
question:

"The truth is that no one can to-day prove t
nitro-carbide rather than a phospho-carbide, a chr
bide, a mangano-carbide, a titano-carbide, a tun
But among these classes of steel, so numerous and
it is the *typical steel*, the *ferro-carbide steel*, which is
gether with the carbon, and which generates the ot
the influence of all the metalloids or the metals wh

Meanwhile, before the third note of Margueri
the Academy of Sciences, Caron had presented
communication in which he reports some ne
to show how pure carbon monoxide *does not cemen*
while *at a lower temperature* (not high enough to so
passing, in contact with iron, into carbon dioxid
this, according to Caron, the cementation (always
gueritte was not produced during the heating *at redr*

We shall see later how the results of Caron's expe perfectly without in any way weakening the validity of

To Caron's observations, Margueritte made answ again citing his earlier experiments but adding conce more details, by which the objections of Caron are cle

The answer of Caron[2] is based first of all on the well-known fact that the carbon employed in industrial *exhausted* with use, becoming incapable of carburizing i not be explained, according to Caron, if the assertion exact that "carbon and carbon monoxide (formed by th carbon of the cement and the oxygen of the air occlud sidered as the most abundant and most active elements tion." In fact, it is clear that, however much the carbo the carbon nor the air occluded in it can suffer any maintains, on the other hand, that it is evident that already used for cementing, the alkalis (contained in of giving rise to the formation of cyanides) have been for the greater part, the diminished carburizing effi is proof of the preponderant action of cyanides in the p

To this observation Caron adds the results of some iron bars in the form of parallelepipedons, 10×10×30 hours to redness in a current of pure carbon monoxide of cementation, while identical bars of the same iron, c cal conditions) with one of the ordinary cements, were a depth of about 3 mm.

Margueritte again answers in two notes, presente of Sciences at the meetings of October 31, and Noven first Note[4] he merely communicates the results of ne gous to his earlier ones), from which it appears tha *temperature* (from cherry-red to light orange) *powder*

arguments, also of a technical nature, which, on t
hypothesis of cementation by simple contact.

As to the diminution of the carburizing efficien
been used as a cement (a diminution which Caron
ization of the alkalis contained in the ashes), he ex
known "change of state" which carbon undergoes
longed ignition, a change which renders it less re
"by contact" or with carbon dioxide to "regenerat
this would confirm precisely the opinion that the di
that of carbon monoxide are preponderant in the
Margueritte points out then that Caron himself, in
to admit (which he would not do at first) that
monoxide can produce, under certain circumstances

After the publication of a note[1] in which, from t
action of retort carbon, he maintains that he can d
of his theory of cyanides, Caron resumes the disc
In the meantime Jullien, director of a steel works, h
citing[2] some facts observed by him in industrial p
they confirmed the assertions of Margueritte co
efficiency of carbon alone, demonstrated that pure
cement iron.

In his next reply Caron,[3] first of all, calls atte
experiments are in full accord with the absolutely n
1859 with minute care by Percy to cement iron wit
Then he refutes the hypothesis of Margueritte, th
burizing efficiency suffered by carbon with use is
density and the diminution of its combustibility, by
coal, used in industry as the most efficient cement, i
and least combustible. Such maximum efficienc
evidently incompatible with the hypothesis of M
firmation of Caron's theory, since numerous analy

monia) is such as to exclude absolutely the possibility
carbon monoxide.

The note ends with a reference to some experiments
that pure sugar carbon, freed from occluded gases by
ignition, does not carburize iron except at a temperatur
melt the product of the carburization (steel or cast iron), b
process of carburization is no longer a cementation. A
made by Margueritte with diamonds, they do not allow
clusion concerning the true processes of cementation, for
for establishing *a priori* that the diamond should behav
same way as ordinary carbon.

Finally, this first polemic concerning the function of
bon monoxide in the process of cementation is conclud
Margueritte.[1] In this, Margueritte begins by maintaini
results of Percy's experiments, cited by Caron, are due
English metallurgist had worked with too slow a current
(three-fourths of a liter in three hours), so that the presen
prevented the cementation.

As to the other experiments of Percy, likewise cited by
declares that the fact that two sheets of iron heated in
current of hydrogen, one in contact with sugar carbon
are both cemented proves, to be sure, that under these
tions hydrocarbons are formed which also cement the sl
contact with the carbon; but Caron has forgotten to say
experiments the iron placed in contact with the carbon i
intensely cemented than that exposed only to the action
constitutes a clear proof that carbon also exercises a mar
ing action *by contact*. And the farther fact observed by
sugar carbon, heated to the melting point of the iron, no
by contact, confirms Margueritte's hypothesis as to the

arguments cited by Caron and supported by his it is a far cry between such a suspicion and the c with which Captain Nicolardot, in the memoir t concludes his summary of Caron's investigations o trouvaient réfutés tous les arguments de Margueri avait affirmé que le carbone pur (le diamant) et pouvaient transformer le fer en acier." ("Thus ar of Margueritte, who was one of the first to affirm th and also carbon monoxide could transform iron

That the assertion of Nicolardot is too absolut becomes still clearer when we study the memoirs of on the basis of the experimental and theoretical metallurgical science. We shall see, in fact, that i find, together with some correct observations contai in the works of Margueritte a large number of expe the basis of a valid refutation of Caron's theories later. For the present it suffices to recall that a contained in the cementation boxes, published in 1 reveal the presence of either cyanogen or cyanides

In the meantime, and in the years following th oirs summarized above, a series of accurate inve to H. Sainte-Claire Deville, Troost and Cailletet, at a high temperature, is easily permeable to variou ever probable that the penetration of carbon into to the diffusion of the carburizing gases into this ma

The problem of the course and nature of the p again taken up a few years later by R. Mannesm the results of his numerous and accurate in published in 1879 under the title: "*Studie* *process*."[2]

While we must consider somewhat exaggerated t

are those composed essentially of iron and carbon, it is
that the process of cementation consists of the simple diffus
into the iron. Mannesmann then subjects to a brief cri
the experimental data already established at the time and th
founded on them. From this examination he concludes th
to the fact that Margueritte's experiments on cementation
with the solid carbon (which had furnished the complete p
of cementation based on the hypothesis of the molecular
carbon) were not extensive and deep enough, and receive
for many years, that the tendency has become general to
theory, better studied from both the theoretical and the e
of view, of the necessity of the intervention of gases in the p
burization of iron.

With this premise, Mannesmann proposes to determine

1. Within what limits of temperature and of carbur
can take place.

2. With what means cementation can be obtained ex

3. Through what process it really takes place, in pract
tion furnaces.

4. What cementation agents are best adapted for any
and how steels of different hardness behave in cementation

In order to avoid a repetition of the contradictions so fre
in the earlier researches between the results of experiments
oratory apparatus and of those executed in apparatus emp
Mannesmann's experiments were all carried out in the works
tions as near as possible to those under which the industrial
executed. I shall have occasion, later, to make some obs
method adopted by Mannesmann and later followed by oth

To answer the first of these propositions, Mannesmann
of experiments consisting in heating in a crucible *at a very*

The examination of the products obtained in th established also two interesting facts: the first is that th cast iron and of steel are distinctly separate from each o the concentration of the carbon, while remaining app

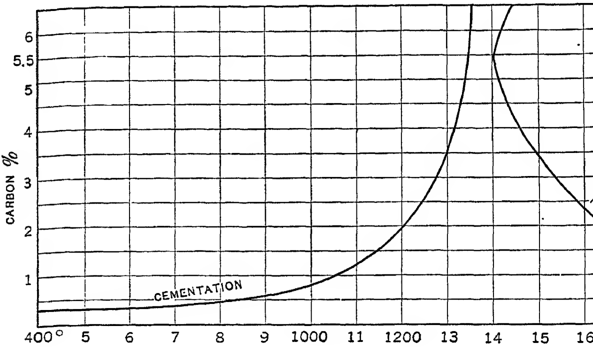
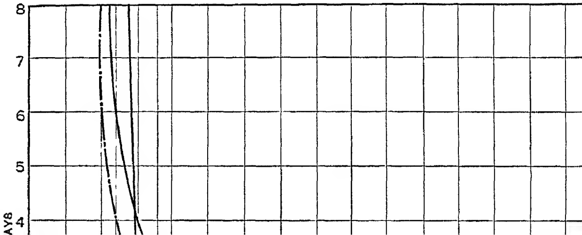


FIG. 7.—Diagram of the formation points and of the fusion po

for any given layer, changes suddenly in passing from to that of steel and, sometimes, directly from cast iron fact (which Mannesmann maintains is proved by his ex



tion) concentration of carbon. These facts are represen Mannesmann in two diagrams, reproduced as Figs. 7 an

As to the lower limit of temperatures at which cementa Mannesmann cites the observations of Caron, according can commence to carburize iron at temperatures much l

Passing to the experimental study of his second ques carries out many experiments, the results of which I sum

(*a*) Experiments carried out with petroleum and asp him to obtain intense cementations, showing thus the ca of hydrocarbons even in the total absence of nitrogen;

(*b*) Numerous tests showed that potassium ferrocyan superficial cementation, but that it is ill-adapted to the cementation;

(*c*) Numerous experiments performed by strongly crucibles, at various temperatures and for varying perio iron half immersed in pure graphite powder, with the ot by inert refractory material reduced to grains the size of le that only the iron placed in contact with the graphite is while the portion surrounded with inert material remain same fact also always manifests itself when the part of th in contact with the graphite is allowed to project into the crucible instead of being surrounded with inert ma have exerted a harmful influence in the "regeneration' formed from the carbon monoxide when the latter yields In this case also, the only part of the bars of iron which that which was placed in contact with the graphite.

The same experiments, performed by substituting fo carbon or lamp-black, previously strongly ignited, gave

From these first experiments Mannesmann maintain conclude that the gases which can be formed in the cem taining carbon interpenetrated with air are so dilute (*d*) On shaking in a glazed and perfectly closed high temperature (but below that at which cast i together with turnings of gray cast iron, Mannes marked cementation of the iron. Now he conside same gas contained in the crucible should on the on from the cast iron, to yield it, on the other hand, temperature, so that these experiments prove that the cast iron is due simply to contact. We shall se the reasoning upon which is based this conclusion shall see also how the deductions drawn by him f periments, intended to confirm the preceding ones, c to those of Series *c* by substituting in these (as in t turnings for graphite, are not exact. In these exp iron were cemented only in the portion placed in dir iron turnings, while they remained unchanged in t the inert granular refractory material.

(*e*) Various samples of iron immersed in *spie* enough to make it pasty, without melting it, were al to depths of 1 or 2 mm. Since the sharp ar iron showed that they had not suffered even a tra "pastiness" of the *spiegeleisen*, which Mannesman trate into spaces 1/2 mm. wide between a series o in it, excluded the possibility of its penetration into of the compact iron," these new experiments cons tion of the possibility of cementation *by contact*, an cular migration" of the carbon into the solid steel.

(*f*) In order to exclude entirely the action of Series *d* were repeated by filling the crucible with fi melting at the temperature of the cementation, c stices between the fragments of cast-iron turnings a tory material. In these experiments also, and in

solid steel, this does not appear, according to Mannes
"theoretically inexplainable," which he proposes to dem
of interesting considerations based on the absence of a lim
cation between the solid state and the liquid state.

Mannesmann observes that iron at the temperature c
be considered as an extraordinarily viscous true *liquid* in
of the molecules is shown by the evidence of the te
manifest to assume the disposition corresponding to
structure, characteristic of iron kept for a long time at a

We shall see later how the considerations developed l
partly confirmed by recent studies, also based on phenon
themselves in many other metallic alloys. Mannesman
to an analogous process of molecular migration must
variations in concentration which (especially as a resu
Boussingault) it has been shown are undergone by v
foreign substances contained in steel, such as sulphur,
arsenic, etc. This is especially evident in the case of
intervention of gaseous compounds cannot be assumed.

Having exhausted thus the examination of the first t
nesmann begins that of the third, proposing to determi
process of cementation is actually effected in practice.

After having confirmed his conception of the preponc
action of carbon by contact, he proposes, by means of a
ments, analogous to those which I have just cited in Seri
under conditions nearer to those which prevail in pra
individual phases of the process of cementation. To thi
cementation box eight bars of iron, removing them one af
the space of thirteen days and a half. The examinatic
thus treated allowed him to establish how the concentr
in the cemented *crust* varies with the progress of the cer
the *velocity of penetration* of the carbon varies in the succ

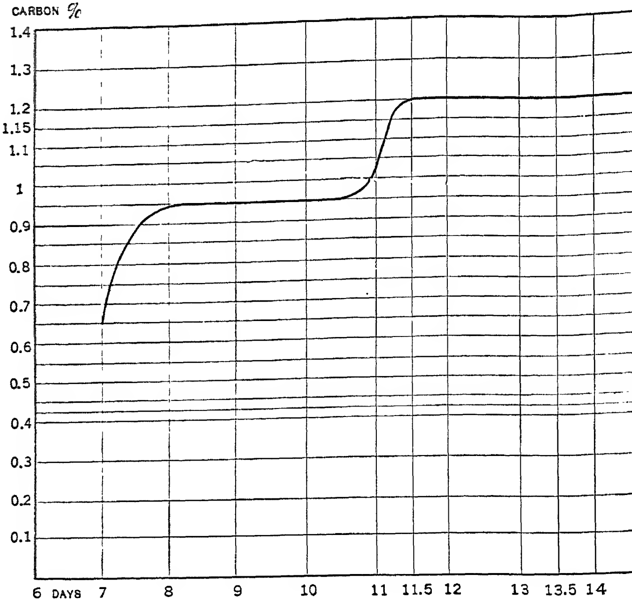
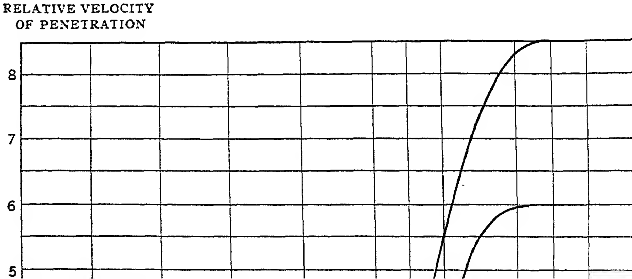


FIG. 9.—Carburization in the various phases of the cementa



zation of the alkalis necessary to form cyanides, which, acco essential for the production of cementation, while Marguer by a more compact "atomic structure" which the carbon result of prolonged heating. From a series of experiments, however, based on the varying effects which are obtained in wood charcoal with nitric acid, according as *new* carbon or c already been strongly heated for a long time is used, Mann that he confirms the hypothesis of Margueritte.

Finally, passing to the treatment of the fourth questio begins by observing that possible improvements in the indu cementation must tend essentially toward a diminution of process and the securing of the maximum homogeneity of the

This granted, he takes as a starting point a conceptio transformed and limited, has, we shall see further on, recently

According to Mannesmann, when the process of cemen not effected by the use of free carbon but with a compoun *degree of carburization* is proportional to the difference betv of the carbon for iron and the affinity of this carbon for the which it is combined, so that, at a given temperature, no com can yield as "high" carburization as that which can be ob carbon, by means of a sufficiently long contact with the i temperature. And, in confirmation of his assertions, Manne examples, to which we shall have to refer later: that of cyanid ied by Caron, and that of carbon monoxide.

To these considerations he adds others, in great detail, consequences of the fact, considered by him as evident, tha due to the direct carburizing action of gases the *regenerati* gases within the pores of the metal can be effected only wit when the carburization has extended to a considerable dept the great friction opposed to the circulation of the gases in

use of cements with a solid carbon base, on the other
economical in the cases where deep cementations and h
to be obtained.

As to the varying carburizing action of different ki
mann cites only the few data (which he himself cons
sented in the diagram reproduced in Fig. 8; these refe
necessary to completely cement bars of iron 12 mm.
coke, wood charcoal or graphite.

The memoir of Mannesmann also contains the re
tions on the formation of "blisters" in steel subject
the basis of these results, the author considers it prov
due solely to the action of the carbon which "migrate
the particles of slag contained in the metal.

Then follow some interesting applications of the
in the preceding pages to the study of the best tech
which it is advisable to carry out the process of cemen
tical cases. To these considerations we shall have oc

Finally, treating the last part of the questions p
studies the behavior of steels of different hardness su
Starting from the conception, already enunciated, that
ture corresponds a definite concentration of carbon
saturated with this element, and that the affinity
(and hence the intensity of the process of carburization
therefrom) is smaller the nearer the steel is to the
Mannesmann maintains that the velocity of ceme
greater the initial concentration of the carbon in
cementation, and since, on the other hand, it is clear t
of cementation the *work of cementation* necessary to rea
the higher the content of carbon started with, it is
conclude that steels of different hardness must b

reciprocal action at high temperature of layers carburized t observations which make evident the tendency which, at the carbon of contiguous zones, carburized to differer migrate from the more highly carburized zone to that whic burized. It is not necessary to repeat here the minute co Mannesmann develops in regard to this phenomenon.

Finally, Mannesmann summarizes the consequences w result from his way of interpreting the many experiments foremost the conclusion that in the process of cementation the carbon into the deep layers of the iron is due essential *migration* of the carbon, while the carburization due to carburizing gases into the iron plays but a small part in th tation and is limited solely to a superficial zone of small de

It is well to note that the same conclusion had been before by Boussingault. The latter, in the course of t already referred to,[1] in which he had observed the varia tion of the other elements (especially sulphur) in the iron s tation, had called attention to the fact that although Caill the gases contained in the cementation chambers from 14% monoxide (a gas of which Boussingault says *its carburiz known*), yet, "considering the quantity of carbon necessar steel the 13,000 or 14,000 kg. of iron contained in boxes," it must necessarily be assumed that the carbon ab during the cementation comes for the most part from the wood charcoal. We shall see later how this argument of supported by a more accurate examination of the phen place in the cementation boxes.

The researches of Mannesmann may be considered a the first period of investigations on the cementation of ste scientific data and methods. To this period, which comp

and which to some may appear too minute. But t
ing memoirs which, containing no facts essenti
considerations to which can be attributed only a
evident.

To the same period of time belong various work
nature and several patents. Of these, though
an account later, when speaking of the indu
process of cementation.

CHAPTER II

STUDIES ON THE PROCESS OF CEMENTATION DURING T
YEARS OF THE NINETEENTH CENTUR

The first period of scientific investigations on the proc
which I have briefly summarized in the preceding page
more for the activity of the researches and the vivacity o
for clear and certain results, is followed by a second, als
duration, during which but few new experimental data
were brought out in support of one or the other of th
hypotheses which in the preceding twenty years had been
adherents as conclusively proved.

Leaving aside what concerns the advances in the tec
tion, with which we shall deal later, I shall summarize bri
the results of the principal scientific studies on the proc
published during the last twenty years of the nineteenth

A first work, due to Alb. Colson, is published in the
l'Académie des Sciences.[1] It contains no data essentiall
process of cementation proper is concerned, that is, the
into iron. The author tries, instead, to study the recipr
and of carbon from a wider point of view, and believes th
with certainty that, in the process of cementation, the diff
into the iron is accompanied by the reciprocal phenomen
of the iron into the carbon. According to the investiga
relatively low temperatures (the phenomenon manifests its

we find an interesting observation, the importance of v
occasion to see later. This observation, from which
was unable to draw any useful conclusion, either beca
conditions not definite enough or because various theor
to analogous phenomena were not then known, relates t
burization (*refining*) clearly observed in a cast iron *ig*
carbon, that is, subjected to the same treatment which
burization of steel.

Finally, R. Sydney Marsden presented at a meetir
Society held on January 20, 1881, a memoir with the
of the Conversion of Bar Iron into Steel by the Cen
According to this *new theory*, the process of cementation is
of the carbon "in the form of *impalpable powder*" into the
under the action of the high temperature, are "in an exp
state." The diffusion of silicon is due to an analogous
I have cited this hypothesis, the improbability of whi
cause it shows plainly how at that time new efforts were
an explanation of the process of cementation more sati
proposed in the preceding years.

Four years later, W. Hempel, in a memoir entitled
der verschiedenen Modificationen des Kohlenstoffs gegen Eise
tur,[1] maintains that he has been able to prove exper
diamond exercises a carburizing action on iron beginnin
considerably lower than the other modifications of carbo

According to Hempel, then, carbon does not cement i
lower than red heat when the iron and the carbon, pla
heated in an atmosphere of nitrogen freed from the leas

The investigations of Hempel can be considered as
value, at least in so far as concerns the determination
temperature between which the various phenomena are *lo*

The memoir of Hempel concludes with a series of c convincing, in truth, or at least premature, on the between the behavior of "white carbon" (diamond) carbon, and on the analogies which exist between thes behavior which distinguish white phosphorus from red

In a brief memoir presented in 1890 before the Iro W. C. Roberts-Austen reports the results of some ex those of Hempel but carried out by heating electrolyti diamond *in a vacuum*, instead of in an atmosphere of n electric current. Under these conditions the carb manifests itself only at intense redness, and then ap before being placed in contact with the diamond, is fir a vacuum so as to free it from occluded gases.

From these experiments Roberts-Austen draws th truth very *prudent*—that whoever wishes to maintain a third substance is necessary to produce the *combinat* must necessarily assume that to produce to a conside minimum *traces* of such substances are sufficient, such substances which can still remain occluded in the iro careful treatment to which this iron was subjected t solved in it.

In the course of the interesting discussion which Roberts-Austen's memoir, G. J. Snelus called attent direct union of carbon with iron appears analogous *solution* than to a true combination proper,[2] and Sir the results of some of his experiments consisting in about a month a piece of cast iron and one of wrough with each other along two perfectly plane surfaces, each other and covered with sand. But the fact obse siderable quantity of the carbon passed from the cas not constitute a certain proof that carbon can diffus vention of gaseous substances, he proposed to study th burization of iron by means of the diamond, and to de temperature within which this carburization is effect

Working in a current of very pure hydrogen, and iron, and diamonds ignited at redness and allowed to di in hydrofluoric acid, Osmond obtains the following re

1. At temperatures of 1035–1065° C., the carburi means of the microscope, attains in the mass of the ir mm., remaining localized around the points of contac with the diamonds.

2. At temperatures of 1085°–1125° C., the diamon tion of 4 % with respect to the iron) completely dissolv melts, forming an ingot of *white cast iron*.

3. Still working at temperatures of 1085°–1125° C of diamonds equal to 8% of the iron, Osmond obtai perature of fusion of gray cast iron is not reached) a *f* iron to which adhere three fragments of blackened dia graphitic patina containing iron. The iron has ther mediary in the formation of the graphite.

From these results Osmond draws the following co

1. The diamond, as such, does not cement iron, bu tact with this metal at a high temperature it first under *formation* which renders it capable of cementing.

2. The diffusion of the carbon into the iron has, as of the iron into the transformed diamond. This conf different conditions, the observations of Colson to wh preceding pagės.

As can be seen, the observations of Osmond, like out by other experimenters during the period with whic are of exclusively theoretical interest.

To investigations of a very different order, which,

one end of which extends into the central and hottest part o
there touches the end of another similar bar of soft steel (with
on). The other end of the bar of carbon is connected electr
ositive pole of a continuous current generator (Gramme m
egative pole is connected with the end of the steel bar which e
he opposite end of the refractory tube.

By passing through the circuit thus established a current
vith a tension of 7 volts (probably measured from the ends
omposed of the two bars) and continuing the operation f
always at a temperature of about 900°–1000° C.), Garnier o
ar of iron a cemented zone 10 mm. thick. As is seen, the
oteworthy.

On substituting for the bar of retort carbon another bar o
lacing between the two projecting ends of the two bars of s
istance of about 1 cm., a little ground and compresse
oal, at the end of the operation, conducted in the mar
bove, only the bar acting as cathode was found to be cemen

I do not find that further results of investigations analogou
een published.

In a brief Note presented at a meeting of the Iron and Ste
ay, 1896,[1] W. C. Roberts-Austen, after tracing briefly t
cientific investigations on the process of cementation of ste
nteresting considerations:

He begins by asserting that, on the basis of the experiment
te (see pp. 8–13), of Hempel (pp. 26–27), of Osmond (se
f his own, it must be considered as proved that the process o
f steel is a true phenomenon of diffusion "by contact" of th
nto the iron, analogous to the process of diffusion of salt into w
f the diffusion of gold or of platinum into solid lead.[2]
oberts-Austen notes how the determination of the *way* in whic
f the carbon into the iron takes place would without doubt be

Roberts-Austen sees a confirmation of his earlier obser of the conclusion that the technical process of ceme simple diffusion of the *solid* carbon into the *solid* iron in contact, without the intervention of gaseous carbu

We shall see later how the conclusions which Robe the examination of this curve and of the two or three a by him later are not at all in accordance with the s from the observation of many curves relative to ceme working under conditions which are simpler, can be d accuracy, and vary between wider limits.

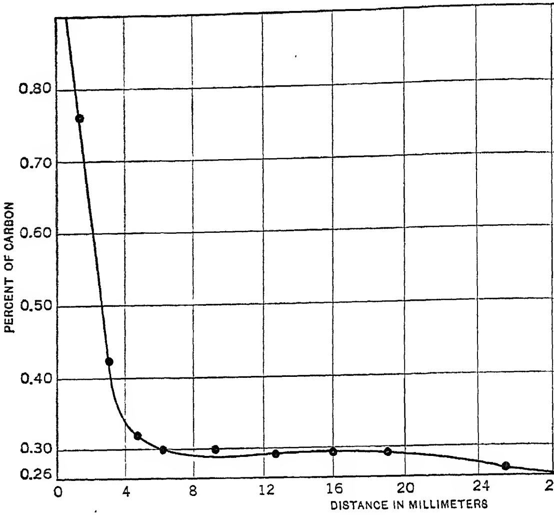


FIG. 11.

Continuing the summary review of the scientific process of the diffusion of carbon into iron, we fi soft steel with 0.15% of carbon together with a bar of hard st carbon, he was unable to observe any change in weight or i in the bars whenever these bars were so placed that they we with each other. On the other hand, working under the but placing the more highly carburized bar between the c contact with them, he found that the aggregate mean carbc first bar had decreased to 0.42%, while that of the other tw rising from 0.15% to 0.29%. This experiment proved, evide ness of the hypothesis according to which carbon diffuses solutions, by simple difference in concentration and withou the intervention of gases.

Together with various other observations on the limit carbon in iron at various temperatures (observations on the regards as confirmed the existence of the two carbides F already announced by others but later recognized as bei Royston maintains that below the temperature correspond Ar_1 carbon no longer tends to diffuse into iron. We shall s conclusion has also been confirmed by more recent experin

To the argument, already considered by Royston in the of the limit of saturation of *solid* solutions of carbon in iron, a memoir presented at the next meeting of the Iron and This limit of saturation, which at a temperature of 700° according to Royston, to 6.9% of carbon, reaches at 900° the experiments of Saniter, the value of 2.95%. In the Saniter, carried out by heating at 900° C. wire of soft stee wood charcoal for more than twenty hours, 0.53% of the ca the graphitic state.

We shall see later how recent studies on the conditions systems consisting of the carburizing mixtures used as cemen tite—free or in the state of solid solution in γ-iron—throw a causes of the contradictory results obtained from the experi

Osmond observes first that the limit of carburization
temperature merely represents the solubility of the ca
at that temperature. This limit, at the temperature
670°), seems to correspond to a carbon content of abo
with rise in temperature. If every limit of carburiza
to a definite compound (which some authors seem to a
to be an infinite series of such compounds, which wo
to the nature of definite chemical compounds. In pra
mental determination of the limit of carburization a
could be carried out by means of direct cementatio
condition of maintaining the temperature rigorously
entire duration of the experiment. In fact, every
temperature would produce the precipitation of a certa
tite, so that from the total quantity of cementite found
of the cementation it would be necessary to subtract t
during the cementation as the result of oscillations
Moreover, the dissociation of the carbide Fe_3C and the
graphite complicate the phenomenon still more.

A year later J. O. Arnold read at the fall meeting
Institute (Stockholm, 1898) an interesting memoir on
of Cementation."[1] This memoir has essentially as i
the processes of carburization which are applied in the in
tion of hard steels of superior quality from the pu
means of total cementation and subsequent crucible fu
I shall have occasion to refer to some of the data cont
when, later, I give a review of the industry just menti

After an interesting notice on the data and methods
the industrial application of cementation to the total
irons into steels of various grades, Arnold reports a serie
microstructure and the chemical composition of the su
cemented bars, belonging to the various "grades,"

made on the successive strata of the bars observed. A
graphy, carried out by Arnold with great care and grea
teresting conclusions might have been drawn to whic
could not have led, because they were carried out on suc
great thickness. Thus, to cite but one case, in one of A
(the sixth) appears most clearly the sudden variation in
carbon which manifests itself at the point correspondi
contact between the hyper-eutectic stratum and the e
cemented zone. We shall see later the practical import

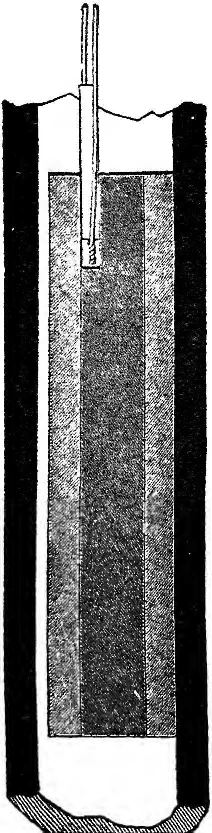
The microscopic observations which I have just cit
firmations of the results of the quantitative determinatio
Arnold on the successive layers (0.02 to 0.04 inch thick)
of the various "grades," and, in turn, the conclusion
results are limited to the establishment that in the deepl
bars the concentration of the carbon is nearly uniform t
metallic mass, while in the bars only superficially cemen
tent diminishes rapidly from the surface layers to tho
For these latter bars Arnold notes briefly in a table th
three distinct strata, but the description and the photo
which he gives of the microstructure of these strata exc
of these with the three characteristic strata (hypo-eute
eutectic) which I shall take up later.

The results of the carbon determinations are collecte
diagrams (diagrams which, in what follows, I shall call
depth diagrams), in which the distances of the median sur
strata from the external surface of the steel bar are plott
the ordinates are proportional to the carbon content of
reproduce these diagrams here, because Arnold does not
from them any but the very simple conclusions which
above.

Arnold's me r concludes with some brief "physic

cementation beyond 0.9% of carbon (a value co
pound" $Fe_{24}C$) and to obtain more highly carburiz
carry out the cementation at temperatures above

The reading of Arnold's memoir was followed



which Roberts-Austen dec
pothesis, based on the exis
carbides $Fe_{24}C$ and Fe_3C,
considers, on the other han
pothesis (which, as we hav
proposed by him) that the
solid steel is a phenomen
that of the diffusion of a sal
adds some observations on
"agglomeration" of cemen
in the prolonged heating of
entation.

The results of the more
Arnold and of MacWilliam,
Arnold which I have just su
ject of another paper, prese
and Steel Institute, in the f
think it well to give a rather

After a brief historical i
mentioned the principal of
the diffusion of carbon into
mond), of iron sulphides i
of gold into lead (Roberts-
scribe minutely the experi
by them for the exact qu
chemical and micrographic
gration" of the various ele

was bored a hole to receive the joint of a thermo-electric cou determination of the temperature of the system; the latter in a porcelain tube which had been evacuated as completely

After heating in a vacuum ten hours at a temperature be 1050° C., the piece, after cooling, was again turned on the lath rial of the muff thus removed until there remained of it on layer one-twenty-fifth of an inch thick. Then the materi was also removed, collected separately and analyzed to es the foreign element contained in the core had penetrated in

On the basis of a first series of experiments, the results c lected in the following table, the authors divide the elen most frequently found in steels into two classes: "migrator "fixed elements."[1]

The microscopic examination of the pieces subjected t described, and numerous control experiments, confirmed t marized in the accompanying table.

Elements		Original percentage in the muff	Original percentage in the core	Percentage in t layer (1/25 inc of the muff ad cent to the co after the trea ment
Migratory	Carbon.......	0.05	1.78	0.55
	Sulphur......	0.02	0.97	0.12
	Phosphorus...	0.015	1.36	0.11
	Nickel........	none	1.51	0.11
Fixed	Manganese....	0.05	1.29	0.04
	Silicon........	0.027	1.94	0.028
	Chromium....	none	1.10	none
	Aluminium....	0.02	1.85	0.02
	Tungsten.....	none	1.41	none
	Arsenic.......	0.02	1.57	0.012
	Copper.......	traces	1.81	traces

lathe the material of *eight* concentric layers (four from the muff and four from the core), the material of each layer being collected separately and analyzed.

The results of the carbon determinations on the eight layers of each of the three cylinders are represented schematically in Fig. 13 and reproduced in three diagrams (Fig. 14), in which the abscissas represent the distances of each of the layers analyzed from the axis of the metallic cylinder and the ordinates are proportional to the corresponding concentrations of carbon resulting from the analysis of this layer.

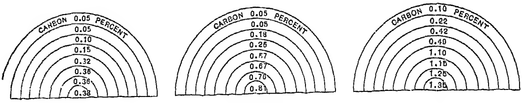


FIG. 13.

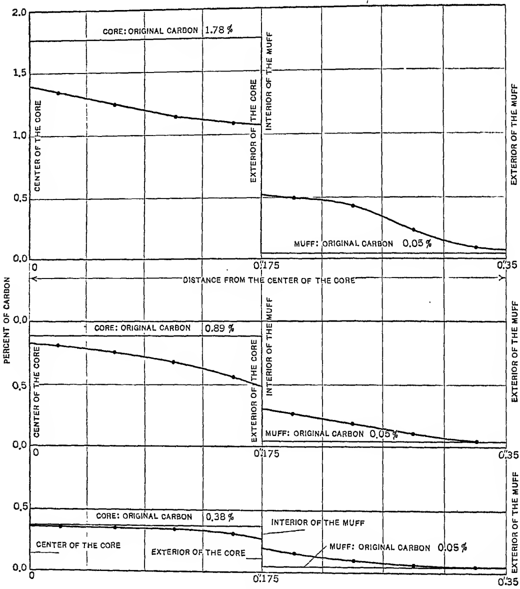


FIG. 14.

From these first experiments the authors limit themselves to drawing the conclusion that the diffusion of the carbon from the core to the muff is the more rapid the higher the carbon content of the core, but they do not find that a simple relation exists between this percentage and the velocity of diffusion.

Another series of experiments, carried out under conditions entirely analogous but working at different temperatures and using successively muffs of iron containing varying percentages of carbon, furnished the results in the following table.

Percentage of carbon in the muff	Percentage of carbon in the core	Length of heating in vacuum (hours)	Temperature (save oscillations of a few degrees)	Percentage of carbon in the layer (1/25 inch) of the muff adjacent to the core after the treatment	Percentage of carbon migrated by diffusion in 6 hours
0.05	1.78	6	636° C.	0.05	none
0.05	1.78	6	739° C.	0.05	none
0.05	1.78	6	785° C.	0.16	0.11
0.05	1.78	6	855° C.	0.45	0.40
0.59	1.78	6	750° C.	0.76	0.17
0.59	1.78	6	850° C.	0.87	0.28
0.89	1.78	6	740° C.	0.87	none
0.89	1.78	6	850° C.	0.87	none
0.89	1.78	6	960° C.	1.20	0.31

Since the determination of the critical points of the metal (with 1.78% of carbon) forming the core shows that this metal undergoes its allotropic modifications at temperatures below 700° C., and does not suffer further transformations above this temperature, and since, on the other hand, the data in the last table show that the most marked variations in the diffusion velocity of the carbon appear at temperatures above 700° C., it is necessary to admit that these variations are due to the "molecular transformations" of the iron constituting the muff.

From the numbers in the table relative to the first two series of experiments (carried out with muffs containing, respectively, 0.05% and 0.59% of carbon) and taking into account the critical temperatures of the two materials constituting the muffs, the authors consider it as proved that the diffusion of the carbon occurs only at temperatures above those of the point Ar_2 of the metal of the muff.

The results of the third series of experiments prove, then, that when the concentration of the carbon in the muff exceeds 0.89% (a concentration for which, according to a hypothesis advanced previously by Arnold, the steel consists entirely of the "subcarbide" $Fe_{24}C$) the minimum temperature at which the diffusion can take place shows a sudden rise of 150° C. (from 750° to 900°).

Such a sudden rise is explained, according to the authors, by assuming that, until the concentration of the carbon in the muff falls below 0.89%, the carbon diffuses in the form of the carbide $Fe_{24}C$, at all temperatures above Ar_2, while as soon as the concentration reaches 0.89% and the entire muff consists of the "subcarbide" $Fe_{24}C$, then the carbon diffuses in the form of the carbide Fe_3C, which is the reason the diffusion can take place only at a temperature above 900° C. Inversely, then, the sudden variation in the minimum temperature of diffusion of carbon is, according to the authors, a proof that the carbon actually diffuses in the two cases in the form of the two different carbides.

For the results of this series of experiments also, the authors advance proofs based on the microscopical observation of sections normal to the axes of the various compound cylinders.

Having reached this point, the authors avail themselves of the experimental results obtained to advance a theoretical explanation which can mostly no longer be accepted to-day, since the non-existence of a definite carbide $Fe_{24}C$ has been proved. They developed, however, some interesting considerations (confirmed, also, by new experiments) on the phenomenon of the diffusion of carbon manifesting itself in the various structural elements of steels during the heating which precedes tempering, and on the effects of such phenomena on the properties of the tempered steels. But the greater part of these considerations, too, though very ingenious, are based upon the supposed existence of the "subcarbide" $Fe_{24}C$; they can not therefore be considered as correct to-day. Moreover, they concern only indirectly the mechanism of the process of cementation.

The memoir of Arnold and MacWilliam closes with some experiments on the diffusion of the sulphide and oxysulphide of iron through iron at high temperatures; the results of these experiments confirm those previously published by Campbell in proof of the great rapidity with which the diffusion of the oxysulphide is effected, and show that the sulphide of iron also, under analogous conditions, diffuses rapidly into iron.

In the discussion which followed the reading of the memoir of Arnold and MacWilliam, Stead raised some objections to the hypothesis that in the process of cementation carbon diffuses into the iron in the form of two definite compounds, $Fe_{24}C$ and Fe_3C, and added some interesting observations (which I do not quote, as they bear only indirectly on the special argument which we are dealing with) on the experiments of the authors and the earlier ones of Campbell on the processes of diffusion of the sulphide and oxysulphide of iron.

Among the observations made by the different speakers in the course of this discussion, in which R. A. Hadfield, Harbord, Stansfield, H. Louis and Saladin participated, those of Harbord are especially interesting: Basing his remarks upon the analogy between the separation of cementite from steel and the crystallization of hydrates from saline solutions, he combats the hypothesis that carbon diffuses into iron in the form of a definite carbide. The observations of Stansfield are based on the same comparison with the crystallization of saline solutions, observations still valid to-day, which bring out with extraordinary clearness the true course of the phenomena which take place during the cooling of steels, as appears on the basis of the most recent experiments, and oppose serious objections (recognized to-day as correct) to the theory of the existence of two distinct carbides of iron ($Fe_{24}C$ and Fe_3C), on which Arnold and MacWilliam base their explanation of the phenomena observed in their experiments. As to the fact observed by the two authors that in a steel with 0.05% of carbon the diffusion of the carbon does not take place to an appreciable extent except at temperatures above 750°, Stansfield explains it very easily and without having recourse to the hypotheses of Arnold and MacWilliam, observing that in such a steel, at 700° C., only about 6% of the mass of the metal (and precisely that part which, in the cooled steel, constituted the pearlite) passes into a state of solid solution (into β-iron), distributed around the crystals of pure iron (α-ferrite), so it is quite natural that under such conditions the diffusion of the carbon, occurring over such a small portion of the mass of the steel, should take place only to a small extent.

Stansfield concludes that further diffusion experiments, analogous to those of Arnold and MacWilliam, may furnish a useful method for determining the solubility curve of the carbide Fe_3C, a curve very difficult to trace by thermal methods.

H. Louis observes that the characteristic behavior of nickel diffusing into solid iron may be due to the formation of nickel carbonyl. He then adds a few observations on the behavior of phosphorus.

The report of the oral discussions, concluded by two very vivacious and not at all objective replies by Arnold and MacWilliam, is followed by two letters, the first of which, by T. W. Hogg, contains some interesting observations which bring out the practical importance of an accurate study of the diffusion of the various elements into steel as a basis for a better knowledge of the phenomena of liquation which manifest themselves in steel ingots.

The second letter, by E. H. Saniter, contains some observations on a possible hypothetical relation between the "diffusibility" of the various elements into solid steel and their atomic volume, and some considerations on the conditions of existence of iron carbides in solution in iron.

The memoir of Arnold and MacWilliam is abstracted fully by Ledebur in *Stahl und Eisen*, July 1, 1898, adding to the summary various considerations of his own.

Like Harbord and Saniter before him, Ledebur considers improbable, and not necessary for the explanation of the facts observed, the hypothesis of the existence of the definite subcarbide $Fe_{24}C$, assumed by Arnold and MacWilliam. Ledebur cannot understand why they seek to attribute to the hypothetical existence of carbides the phenomena of the diffusion of carbon into solid iron, both in the case (used in the process of cementation) where the diffusion takes place by contact of the free carbon with the iron and in the case where the diffusion is effected between more highly carburized iron and that less carburized, placed in contact. He maintains that the same phenomena are explained very simply by the passage of the carbon "from the molecules which are richer in it to those which contain a smaller amount," by a process entirely analogous to that of diffusion in saline solutions.

CHAPTER III

STUDIES ON THE PROCESS OF CEMENTATION DURING THE FIRST SEVEN YEARS OF THE TWENTIETH CENTURY

The last period of scientific studies on the process of the cementation of steel is clearly distinct from the preceding one, being characterized by the fact that the experimental researches comprised within it were almost always carried out with new and more accurate means of investigation, and interpreted on the basis of the new theories of physical chemistry.

Another fact characteristic of this period, which includes the first decade of our century, is the renewed activity in scientific researches on the cementation of steel, a fact which, however, is explained quite easily by the recent rapid development of the mechanical industries (and especially of the automobile industry) for which (as we shall see later) the process of cementation is becoming every day a more valuable and necessary aid.

The period with which we are now dealing can be divided into two well-defined parts:

In the first, which includes the first seven years, many of the old problems which we have seen in the preceding chapters studied and discussed for many years back, are subjected to new, ample and accurate investigations, carried out with new experimental methods and interpreted according to the new physicochemical doctrines. But the work of these first years, while preparing new and valuable experimental material, does not lead yet to the sure and complete solution of the problems studied so many years; among these it suffices to mention that of the definition of the function of solid cements and of gaseous cements, and that of the limits of temperature between which the process of cementation is effected.

In the second part of the same period, including approximately the last four years, several of the fundamental questions of the theory of cementation are completely solved in definite form, various important technical improvements of the process of cementation being based on their solution.

In the present chapter I shall limit myself to setting forth objectively the results of the experimental researches carried out during the first part of this last period, reserving the discussion of the possible theoretical and practical conclusions for one of the following chapters, together with those from the earlier investigations, summarized in the first two chapters, and of the later, more important ones, summarized in the fourth chapter.

Leaving aside some works of entirely secondary importance or of exclusively technical character (of the latter we shall speak later), the first important scientific investigations on cementation carried out during the last decennium are due to G. Charpy.

Charpy's studies mark the beginning of the new period of active scientific investigation on the process of cementation.

The first paper on cementation by Charpy was published under the title: *Sur la cêmentation du fer.*[1] In it the author begins by pointing out how, notwithstanding the great number of previous *qualitative* investigations on the process of cementation, the only *quantitative* determinations on this process are those carried out by Mannesmann who (as we have already seen) had tried to establish the content of carbon which limits, at various temperatures, the cementation of the iron. But the series of temperatures determined by Mannesmann certainly contain inexact data, since in them the temperature of fusion of iron is put at 2000° C.

Charpy then reports briefly his results obtained by cementing iron filings, turnings and wires by means of a series of different cements: graphite, wood charcoal (ignited or fresh, pure or mixed with alkaline earth carbonates), animal charcoal, illuminating gas, carbon monoxide, cyanogen, potassium cyanide. The experiments were carried out under well-defined conditions, using, for the heating, an electric furnace with which it was possible to keep the temperature very constant, and measuring the latter very accurately by means of a LeChatelier thermo-electric pyrometer.

On the basis of his experiments Charpy maintains that he has proved that the cementation is not limited by the solubility of the carbon in iron, whatever may be the cement used or the temperature at which the cementation is effected.

"When the metal subjected to experiment is saturated with carbon, which happens after an interval of time which is a function of the dimensions of the specimen of steel, of the nature of the cement (which furnishes more or less carbon in the unit of time), and of the temperature (rises in which increase the velocity of diffusion of the carbon), crystals of cementite, or carbide of iron, can separate at certain points of the metal; they develop gradually on account of the inevitable oscillations of the temperature, which is kept *physically* constant.

"It is possible, therefore, even though the solubility of carbon in iron corresponds to a very low content, to completely transform the metal into carbide of iron, containing 6.67% of carbon . . . ."

I have quoted Charpy's words literally because, as is easy to verify on the basis of what we have already seen in the preceding pages, the observations to which they refer constitute a confirmation, based on accurate experimental data, of the considerations already developed before by Osmond,[2] and therefore lead to conclusions essentially different from what all previous investigators had thought they were able to demonstrate with certainty.

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[1] *Comptes Rendus de l'Acadêmie des Sciences,* 1903, 1st sem., Vol. CXXXVI, p. 1000.

[2] *The Journal of the Iron and Steel Institute,* 1897, Vol. II.

These first experimental results of Charpy have given rise recently[1] to various interesting considerations on the conditions of the formation and of the equilibrium of cementite in the system iron-carbon.

Among the experiments on which he founds his assertions, Charpy cites the following: fillings of soft iron were kept *at a temperature of about* 650° in fused potassium cyanide, portions being analyzed from time to time.

After	48	hours' heating	the	filings	contained	4.50%	of carbon
After	86	hours' heating	the	filings	contained	6.72%	of carbon
After	110	hours' heating	the	filings	contained	6.72%	of carbon

After eighty-six hours the iron was therefore totally transformed into carbide, nor did it undergo any further transformation; the carbide obtained was completely soluble in acids and did not contain a trace of free carbon.

In view of the slowness with which the diffusion of the carbon proceeds at the relatively low temperature (around 650°), "if a piece of metal of considerable size is treated under the same conditions, it is observed that on its surface is formed a layer of iron carbide, almost pure, which cracks at many points when the metal is bent; then comes a layer of variable cementation which is but a few hundredths of a millimeter thick."

Working at higher temperatures, Charpy observed that the iron carbide decomposes, giving graphite. Thus, a piece of steel 3 mm. in diameter, heated for sixty-four hours at 1000° in a current of illuminating gas, gave a product containing 8.32% of carbon, 7.66% of it in the state of graphite. And steel filings heated at 1000° C. in *carbon monoxide* contained after thirty-six hours 9.27% of carbon, 8.27% of it in the state of graphite.

Charpy concludes that ". . . the cementation is not limited by the solubility of carbon in iron. It is possible to obtain by means of it either (when working under given conditions, and especially at low temperature) the transformation of the iron into iron carbide, or (under normal conditions) the indefinite transformation of the carbon into graphite by means of a limited quantity of iron acting as an intermediary."

We shall see later the great importance of the observations contained in this first work of Charpy.

About a month after the presentation of Charpy's Note, a preliminary note was presented by Guillet before the same Academy of Sciences.[2] In this Guillet summarizes the first results of some investigations undertaken by him on the cementation of carbon steels and of special steels, using as cements: potassium cyanide, a mixture of potassium ferrocyanide and bichromate, wood charcoal, a mixture of wood charcoal with 5% of potassium carbonate, various mixtures of wood charcoal and barium carbonate, illuminating gas, animal charcoal.

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[1] See Benedicks, *Ueber das Gleichgewicht und die Erstarrungsstrukturen des Systems Eisen-Kohlenstoff* (*Metallurgie*, 1907, Nos. 12–14).

[2] *Sur la cémentation des aciers* (*Comptes Rendus de l'Académie des Sciences*, 1903, 1st sem., Vol. CXXXVI, p. 1319).

For carbon steels Guillet reaches the following conclusions:

The velocity of penetration of the carbon is independent of the initial content of carbon in the steel, at least for hypo-eutectic steels, increases very rapidly with the temperature, varies for different cements, reaching, however, for many of these, the same limit as is reached, in general, after eight hours of heating at 1000° C. The effectiveness, which we have already seen was observed by Caron, of the addition of potassium carbonate (about 5%) to the wood charcoal is confirmed; this effectiveness Guillet attributes, as had already been done by Caron, to the formation of potassium cyanide by the action of the nitrogen of the air contained in the cementation boxes.

The brittleness of cement steels is due, in part, to the action of the prolonged heating on the "heart" of the steel, in part to the presence of cementite in the cemented zone.

As far as concerns the limit of concentration of the carbon obtained at various temperatures with different cements, Guillet observes that by cementing a fine wire of soft steel at 1100° C., after eight hours about 1.9% of carbon is obtained and the steel has a uniform structure, characterized by the usual network of cementite of highly carburized steels.

On repeating the cementation, the cementite of the network agglomerates and the absorption of the carbon begins again, proceeding, however, very slowly.

Passing then to the study of the cementation of special steels, Guillet communicates two very interesting observations.

1. The simple cementation of steels of considerably high nickel content (more than 7%) makes it possible, when it is continued until there is obtained in the cemented zone quite a high carbon content, in general above 0.8%, to obtain samples of steel, the center of which preserves the structure of tempered carbon steel, while the external layer assumes, *without tempering*, the martensite structure and the hardness of tempered steel;

2. γ-Iron steels (for example, a steel with 30% of nickel) are cemented at temperatures considerably lower than those below which carbon steels no longer undergo any modification.

To these results of the first investigations of Guillet we shall very soon have occasion to return.

A few months later Charpy presented before the Academy of Sciences[1] a new Note "Sur l'action de l'oxyde de carbone sur le fer et ses oxydes," the first part of which contains some data, the importance of which, when completed and interpreted more rationally, we shall see later.

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[1] *Comptes Rendus*, 1903, 2nd sem., Vol. CXXXVII, p. 120.

Charpy experimented by heating iron wire in a slow current of carefully purified carbon monoxide, and determined, in every experiment, the increase in weight of the metal and the quantity of carbon dioxide evolved; then he heated the metal (freed from any deposit of pulverulent carbon) in a current of oxygen to determine the quantity of carbon absorbed by this metal.

Charpy was able to observe that *above* 750° C. no deposit of pulverulent carbon is formed and the metal is sharply cemented, remaining perfectly polished and brilliant. In this case the values of the carburization deduced from the increase in weight of the metal agree with those obtained by the combustion of the metal and with those deduced from the weight of the carbon dioxide evolved during the cementation.

At temperatures below 750° C. a deposit of pulverulent carbon is formed, while the metal is carburized. Charpy maintains that he already obtains a true cementation proper at 560° C.

I reproduce herewith the table of numerical data reported by Charpy, as we shall have to refer to some of these data in what follows.

Temperature	Length of heating	Carbon fixed on the metal		
		Deduced from the increase in weight of the metal	Determined by combustion of the metal	Deduced from the weight of carbon dioxide evolved
560°	8 hrs.	0.10	0.09	Deposit of carbon
600°	8 hrs.	0.22	0.17	Deposit of carbon
715°	8 hrs.	0.26	0.28	Deposit of carbon
825°	3 hrs.	0.56	0.57	0.60
925°	2 hrs.	0.69	0.72	0.60
935°	2 hrs.	0.41	0.41	0.49
1025°	2.5 hrs.	0.60	0.58	0.58
1050°	2 hrs.	0.44	0.47	0.44
1085°	2 hrs.	0.53	0.53	0.58
1125°	2 hrs.	0.46	0.50	0.47
1175°	2 hrs.	0.47	0.47	0.51
1185°	2 hrs.	0.53	0.53	0.47
1190°	2 hrs.	0.30	0.36	0.33

From these data, Charpy maintains that we can at once infer that *the velocity of cementation* does not increase appreciably for temperatures higher than 900°. We shall see later how this assertion, not entirely exact, is due to the fact that in the experiments of Charpy it was not possible to take into account the practically most important factor in the velocity of *cementation*, that of the velocity of *penetration* of the carbon, taken as the depth to which the carbon penetrates into the mass of the iron in a given time. This factor, as well as the distribution of the carbon in the cemented zone, which we shall see is no less important, Charpy could not take into account on account of the shape—fine wires—in which he used the iron subjected to the action of the carbon monoxide.

Charpy observes that this fact can not be due to a phenomenon of saturation, for, as he himself showed in an earlier note, just reviewed, by sufficiently prolonging the contact of the iron with the carbon monoxide the separation of graphite in the metal can be secured. He adds that "the cementation will, on the contrary, be limited if, instead of working in a current of gas, the steel is heated in the presence of a limited quantity of carbon monoxide; under these conditions, the carburization ceases when the proportion of carbon dioxide formed reaches a certain value."

I will note here, since I shall make use of this observation later, how all the experiments carried out by Charpy at temperatures above 900° C. were limited to a duration of two hours (a single one barely extended two hours and a half), so that, a *slow* current of carbon dioxide always being used, all the cementations above 900° C. were in reality carried out with a limited quantity of carbon monoxide.

Charpy's note ends with some brief observations on the action of carbon monoxide on the oxides of iron; interesting observations which, however, bear only indirectly on the processes with which we are dealing.

In the meanwhile Guillet was continuing, from a standpoint somewhat different from that of Charpy, his investigations on the cementation of carbon steels and of special steels; investigations the results of which he had already, in part and succinctly, made known in the preliminary note summarized in the preceding pages. The definite results of this first series of researches are collected into a memoir presented by Guillet before the "Société des ingénieurs civils de France."[1] This it is well to review here somewhat in detail, for, although some of the data and deductions contained in it have been modified by the results of later investigations, nevertheless it has been the starting point of a series of researches and discussions fruitful in useful practical results.

Starting with some considerations on the great importance of the process of cementation and of the empirical data which in general guide and regulate its industrial application, Guillet proposes to "study this process by scientific methods," making use especially of the methods of microscopic metallography, and to "establish for it simple rules, easy to put into practice."

He considers it certain that cementation is produced only with γ-iron, the only one which can dissolve carbon, and that all carbon steels (whatever their content in carbon may be) are susceptible of "taking cementation."

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[1] Léon Guillet, *La cémentation des aciers au carbone et des aciers spéciaux* (*Mémoires et compte rendu des travaux de la Société des Ingénieurs Civils de France*, Series VI, Year LVII, No. 2, February, 1904).

According to Guillet, the course of the cementation is regulated by four factors:[1]

1. The nature of the steel;
2. The nature of the cement;
3. The temperature of heating;
4. The length of contact.

These factors he proposes to study separately.

Beginning with the study of the cementation of the carbon steels, Guillet premises that in the final result of this process two things only can vary:[2]

1. The penetration of the carbon, which may be more or less deep;
2. The concentration of the carbon in the peripheral layer.

The first datum can be determined by means of the microscopical examination of a section of the cemented specimen, suitably polished and etched; and here the author dwells on the explanation of such an examination, recalling the distinction of carbon steels as hypo-eutectic, eutectic and hyper-eutectic,[3] and reproducing four microphotograms of cemented steels.

As to the second datum—the carbon content of the surface zone of the cemented cylinders—it is necessary to determine it by gravimetric analysis (by combustion) of the material obtained by removing on the lathe a surface layer of the metal about a quarter of a millimeter thick.

Guillet always carried out his experiments by cementing, in boxes 8 cm. in internal diameter, cylinders of steel 20 mm. in diameter and introducing the cold boxes into the furnace. He begins by proving, on the basis of a series of experiments carried out with a cement, the nature of which he does not indicate, on cylinders of steel of varying carbon content, that "up to a carbon content equal to at least 0.510%, the velocity of penetration of the carbon is independent of the initial content of this element in the steel."

Then, on the basis of a second series of experiments, also performed with a cement which he does not indicate, the author establishes "that the penetration increases with the time, but it is impossible—at least for the cement used in these experiments—to affirm that the velocity of penetration is constant." He concludes that in practice "it is necessary to test well the cement which is used and to make preliminary experiments as a basis, in order to obtain a definite penetration."

A third series of experiments shows that, all other conditions being equal, the velocity of penetration varies greatly with variation in the temperature, so that in certain cases a difference of 100° C. can double the velocity of penetration. The exact determination of the temperature of the cementation box is therefore of the greatest importance.

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[1] We shall have occasion to see, in what follows, that these factors are, in reality, more than four. Thus, for example, we shall see that to the factors indicated by Guillet it is necessary to add the pressure of the carburizing gas, the manner of the cooling of the cemented pieces, etc.

[2] We shall see later that here, too, other variations can present themselves. It suffices to mention, for example, the *distribution* of the carbon in the cemented zone.

[3] As I have already remarked, I must assume that the reader is well informed on what concerns the metallography of steels.

Finally, Guillet devotes a last series of experimental researches to the study of the influence of the nature of the cement on the course of the process of cementation.

After having noted the necessity of using only cements composed of chemical products of definite composition, so as to be always in a position to reproduce them exactly, and after having given a list of some cements satisfying such conditions, the author examines separately the mechanism of their action, distinguishing, from this point of view, six different cases:

1. As regards cements composed of carbon alone (such as sugar carbon, graphite and wood charcoal), Guillet affirms that important experiments recently completed have permitted him to establish that they *can not act by simple solution of the carbon by the iron placed in contact with them. Pure carbon does not cement in a vacuum.*

2. A cement containing carbon can act by means of the carbon monoxide formed by the action of the air contained in the box. But carbon monoxide *acts slowly*, giving $2CO = C + CO_2$. Moreover CO_2 has, on the contrary, a decarburizing function. In this way will act sugar carbon, washed animal charcoal, etc. To the statements of fact contained in this passage I shall have occasion to refer later.

3. Cements which contain a cyanide (such as potassium cyanide) act by means of the cyanogen group $(CN)_2$, which decomposes, liberating carbon.

4. In many cements the *formation* of a cyanide takes place. Such, according to Guillet, is the case with potassium ferrocyanide (which gives potassium cyanide and cyanate, together with iron oxide), with the mixture of potassium ferrocyanide and bichromate (which gives rise to a mixture of cyanate and cyanide, diluted in a mass of iron oxide and chromium oxide), with the mixture of carbon and barium carbonate (which, in the presence of the nitrogen of the air, gives barium cyanide and carbon monoxide, both active), and finally with ordinary wood charcoal, which owes its activity, above all, to the formation of potassium cyanide by the action of the nitrogen of the air on the potassium carbonate which is always contained in it.

To these considerations also (which are but the confirmation of those which we have already seen developed by Caron) we shall return later.

5. In cements which contain, together with carbon, carbonates which are dissociated at the temperature of cementation (especially calcium carbonate) there is formed carbon monoxide, which reacts, although very slowly.

6. Hydrocarbons, sometimes used in the cementation of large pieces, *certainly act by dissociation.* We shall have occasion, in what follows, to examine this last assertion, which, thus isolated, is not very clear.

On the basis of these considerations, Guillet classifies the cements in the following way:

1. Cements whose activity is due to carbon monoxide;
2. Cements whose activity is due to a cyanide (of potassium, of barium, of ammonium);
3. Cements whose activity is due to hydrocarbons.

The results, reproduced in the two accompanying diagrams (Figs. 15 and 16) taken from the data of Guillet, of a series of cementation tests performed with various cements under varying conditions, show that beyond a certain duration of the operation (about eight hours at 1000°) the velocity of penetration of the carbon is about the same for all cements, while this velocity varies widely from cement to cement at the beginning of each operation.

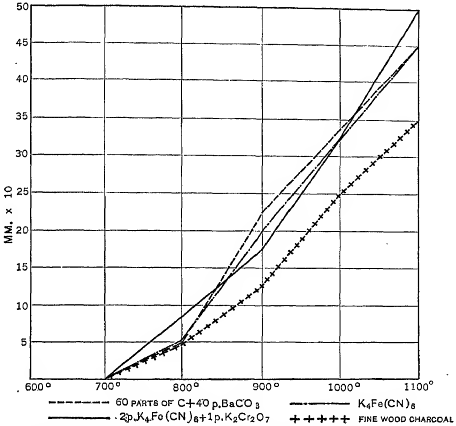

FIG. 15.—Variations in the velocity of penetration of the carbon with variations in the temperature and in the cements. (*Guillet.*)

An exception to the first part of this rule is wood charcoal which (as can also be seen from the two diagrams reproduced herewith) shows the smallest penetration after eight hours' heating at 1000°, while it gives a normal penetration after one hour.

Guillet explains this fact by assuming (as Caron had already assumed) that the carburizing activity of wood charcoal is due to the potassium cyanide which is formed by the action of the nitrogen of the air contained in the cementation boxes on the potassium carbonate always contained in ordinary wood charcoal. The course of various cementations carried out with mixtures of wood charcoal and potassium carbonate successively in a current of nitrogen, in a current of gaseous ammonia, and simply in the presence of the air contained in the boxes, showed that the *exhaustion* of the cement composed of carbon and potassium carbonate is due to the volatilization of the alkali cyanides and not to the exhaustion of the nitrogen contained in the cementation boxes.

In fact, the penetration is the same in the presence of air as in the presence of nitrogen. In a current of ammonia the penetration is continuous and always the same with any cement whatever; which, according to Guillet, is explained by assuming that in every case there is formed ammonium cyanide, to which the carburization is always due.

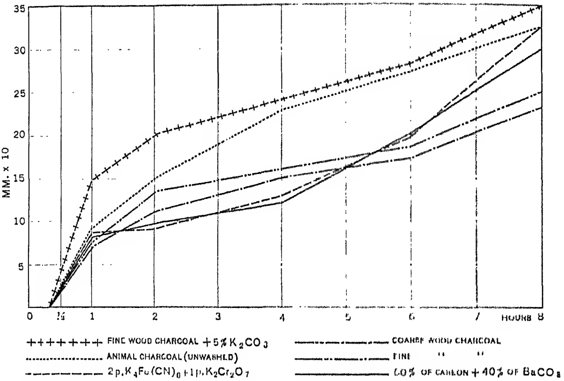

FIG. 16.—Variations in the velocity of penetration of the carbon with variations in the cements and in the length of heating. (*Guillet.*)

This last series of experimental researches on carbon steels concludes with some experiments which show the *influence of the cement on the carbon content of the surface layer.* The results of these experiments are collected in the following table:

Cements used	Carbon content In 1st layer (1/4 mm. thick)	 In 2nd layer (1/4 mm. thick)
80 C + 20 $BaCO_3$	1.14	0.75
60 C + 40 $BaCO_3$	1.32	1.19
40 C + 60 $BaCO_3$	0.94	0.77
$K_4Fe(CN)_6$	0.98	0.81
2 parts $K_4Fe(CN)_6$ + 1 part $K_2Cr_2O_7$	1.06	0.82

At this point Guillet, considering that he has solved with these experiments all the problems which relate to the properties of the cemented zone, passes at once to the study of the effect of the heating which accompanies the cementation on the mechanical properties, and especially on the brittleness, of the part of the cemented pieces ("core" or "heart") to which the carburization does not extend. He concludes (which could easily have been foreseen) that to reduce the brittleness to a minimum it is necessary to cement a steel containing the least possible amount of carbon during the shortest possible length of time and at the lowest possible temperature.

On the basis of various practical considerations, Guillet holds that the best carbon steel for cementation should contain from 0.10% to 0.15% of carbon and *a minimum quantity of manganese.*

A steel containing *more than* 0.35% *of manganese exfoliates* easily on quenching, when it is highly carburized.

We shall see later that the principal cause of the *exfoliation* of cemented steel is quite different from that indicated by Guillet.

The best temperature for the cementation is 850° C., being that which does not make the "core" of the cemented pieces brittle.

Guillet then lays much stress on the great importance of trying to obtain cemented zones in which the carbon concentration of the peripheral layer is exactly that of the eutectic, 0.90%. In this way only is one sure to avoid the presence of needles of cementite, which often do not disappear in quenching and are the cause of very great brittleness in the cemented zone.

We shall see later how this direction of Guillet has an importance even considerably greater than that attributed to it by its author.

It is necessary, then, to avoid "sudden cements," that is, those which in a short time give a surface layer rich in carbon. To this end Guillet recommends a cement, already recommended (as we saw) by Caron since 1861, composed of carbon (60 parts) and barium carbonate (40 parts).

The author then advises making the cementation boxes in such a way that there shall be around the pieces of steel a uniform layer of cement, about 5 cm. thick.

Finally Guillet characterizes as ridiculous the custom, common to almost all works, of quickly quenching the cemented pieces as they are removed from the boxes, for in this way the temperature at which the hardening is done can in no wise be controlled. He advises, instead, letting the cemented steel cool, to bring it to about 800° C., leaving it for the necessary length of time in a furnace heated to this temperature, and then to harden it. We shall see later how this procedure also presents serious disadvantages, and how the most rational process, and the one capable of furnishing the best and surest results, is a combination of that criticised by Guillet with the one recommended by him.

Having exhausted this first part of his investigations relative to the cementation of carbon steels, Guillet completes the series of his practical rules by indicating the conditions which a good cementation furnace must satisfy.

As an example of a rational equipment for the cementation of mechanical pieces, he gives an interesting description, accompanied with photographs and plans, of the equipment adopted by the firm of Fichet and Heurtey in the shops of the Dion-Bouton automobile factory. To these practical data, with which we shall deal later, the author adds some considerations on apparatus for the measurement of temperature in the cementation furnaces; among such apparatus he recommends, for its accuracy and practicability, Féry's pyrometer, which he used in his experiments.

Of the use of this and other pyrometers I shall speak later.

Finally, Guillet passes to the study of the cementation of special steels, and establishes at once that the addition of 2% of nickel to an ordinary cement steel causes the disappearance of the brittleness which such a steel usually shows after cementation.

We shall see later how the great advantages which nickel steels show, as compared with ordinary carbon steels, compensate largely, in fact, for the somewhat higher cost of the former steels as compared with that of the latter.

The author then studies "the influence of various elements on the velocity of penetration of the carbon," subjecting to cementation, all under identical conditions, many special steels containing the same quantity of carbon (about 0.15%).

The results obtained are collected into the following table:

Proportion of foreign metal	Velocity of penetration in tenths of a millimeter	Proportion of foreign metal	Velocity of penetration in tenths of a millimeter
2.0% of nickel	7	2.0% of molybdenum	11
5.0% nickel	5	1.0% titanium	8
0.5% manganese	11	2.0% titanium	7
1.0% manganese	12	0.5% silicon	6
1.0% chromium	10	1.0% silicon	5
2.0% chromium	11	2.0% silicon	4
0.5% tungsten	9	5.0% silicon	0(*a*)
1.0% tungsten	9	1.0% aluminium	4
2.0% tungsten	12	3.0% aluminium	2
1.0% molybdenum	9		

(*a*) No cementation.

Under the same conditions a carbon steel showed a penetration of nine-tenths of a millimeter.

On the basis of these data Guillet considers it proved that "the substances which retard cementation are those which are found in solution in the iron (nickel, titanium, silicon and aluminium)," and that "the substances which accelerate cementation are those which seem to exist in the state of double carbides, substituting a part of the iron of the cementite (manganese, chromium, tungsten and molybdenum)."

Examining separately, next, the behavior of the various types of special steel subjected to cementation, Guillet communicates some interesting observations which I summarize briefly, deferring the discussion of a part of them:

1. **Cementation of Nickel Steels.**—The author lays stress on the observation (already published by him before[1]) that on cementing a steel containing more than 7% of nickel in such a way as to obtain at the periphery a carbon content higher than 1%, there is obtained a superficially cemented zone which, even when not subjected to tempering but allowed to cool slowly, possesses the martensite structure and the hardness characteristic of tempered steels.

This procedure, patented in various countries by the Dion-Bouton Works, makes it possible to abandon the hardening of cemented pieces and hence to avoid all the disadvantages which accompany this operation, such as deformations, fracturing, etc. Extending, then, the carburization so as to reach 1.5% of carbon at the periphery, there can also be obtained a superficial layer, superimposed on the martensite zone, containing γ-iron, easily admitting of polish without loss.

The author reproduces various micrographs of nickel steels cemented by these processes and gives notice that he is prosecuting investigations of this nature.

2. **Cementation of Manganese Steels.**—These steels behave like nickel steels except that, on cementing, for example, a steel with 5% of manganese so that the external layer contains 1% of carbon, "*a pearlite core is obtained, then a little martensite is seen,*" but the periphery is "*characterized by a great abundance of troostite*" and is not, therefore, as hard as that of steel with 7% of nickel. The author adds the diagram of structure of steels with various amounts of manganese and carbon. I do not reproduce this diagram because, together with other analogous ones traced by Guillet for other special steels, it is well known, owing to its importance, to all who deal with special steels.

3. **Cementation of Chromium Steels.**—By cementing a steel with 5% of chromium there can be obtained a martensitic steel, and by sufficiently extending the cementation there is obtained, in the surface layer, a double carbide of iron and chromium.

4. **Cementation of Tungsten Steels.**—The cementation of these steels, which have no practical interest whatever as cemented steels, produces the appearance of the doube carbide of iron and tungsten, or increases the proportion of it in the cases in which it already exists.

5. **Cementation of Silicon Steels.**—Steels containing more than 7% of silicon or those which, while containing a smaller amount of silicon, have been

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[1] I have already reviewed this work on p. 44.

heated sufficiently long, contain all the carbon in the state of graphite; such steels can not be cemented.

6. Steels Which do not Cement.—Besides the silicon steels, whose carbon content (as we have just seen) does not increase on cementation, there are steels whose hardness does not increase, and sometimes diminishes, as the result of cementation followed by quenching. Thus, on cementing a martensitic nickel steel, there is obtained an external layer of γ-iron, considerably less hard than the original steel.

7. Steels which Cement at Low Temperature. In an earlier publication which I summarized above,[1] Guillet had shown that a γ-iron steel can be cemented even at 450° C. by using as cement potassium cyanide, whose melting point is lowered by the suitable addition of alkali and alkaline earth chlorides. Now he shows that the diffusion of carbon into γ-iron takes place even at ordinary temperature; in fact, a γ-iron steel which, cemented at 1000° C., contained at the surface 1.22-1.35% of carbon, after six months contained (always at the surface) only 0.85-0.92% of carbon: the carbon of the pheriphery had therefore continued dissolving into the mass.

The same results, confirmed by some later experimental data, analogous to those just referred to, are summarized in a note presented five months later by Guillet before the "Académie des Sciences.[2]

In October of the same year Charpy published in the American Journal *The Iron and Steel Magazine*,[3] under the title, "Notes on Cementation," a memoir in which are developed at greater length the considerations contained in the two notes which I have reviewed in the preceding pages,[4] presented by him in the preceding year before the "Académie des Sciences." Of this new paper, I shall review only the part which relates to facts and considerations of which the author had not spoken in the preceding papers which I have summarized.

Charpy begins by calling attention to the fact that in the study of the solubility of carbon in iron it is necessary to take into account, besides the solubility of the cementite, that of the graphite also, which is now known with absolute certainty.

Taking up again, then, the attempts, thus far fruitless, like those of Mannesmann, to determine the solubility of cementite in iron, by means of cementation tests, Charpy reports the results of four series of experiments carried out by cementing a wire of soft steel (with 0.04-0.09% of carbon) by means of four cements: wood charcoal, illuminating gas, potassium cyanide and cyanogen.

Notwithstanding all the precautions taken in the execution of these experiments, the results are extraordinarily irregular; the concentrations of carbon obtained vary irregularly from minima of 0.15–0.24% to maxima of 3.5–3.9% without its being possible to find any connection between these values and the conditions of temperature, of quenching, etc., under which the cementation was carried out.

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[1] See p. 44.

[2] *Comptes Rendus*, 1904, 1st sem., Vol. CXXXVIII, p. 1600.

[3] *The Iron and Steel Magazine*, Vol. VIII, No. 4, p. 309.

[4] See p. 44 *et seq.*

Moreover, some of the cemented specimens contain an excess of cementite; others, an excess of graphite. From these experiments it seems that it is not possible in cementation to reach a limit of saturation; nor is it, therefore, possible to determine in this way the solubility of cementite.

Here Charpy recalls his reasoning, which I have already referred to in the preceding pages (see p. 42) to explain the separation of the excess of cementite and acknowledges that, unknown to him, Osmond (see p. 32) had already used (as we have seen) the same reasoning to explain the analogous results of some experiments of Saniter. (See p. 31.)

In confirmation of these deductions, Charpy reports the results of the experiments (which I have already summarized on pp. 42–43) in which filings and fine wires of iron are totally transformed into cementite by means of cementation with potassium cyanide, and others in which the cementation of the same materials with illuminating gas and with carbon monoxide gives rise to the formation of considerable proportions (more than 8%) of graphite.

From these data it follows that the segregation of the cementite and of the graphite occurs only near the point of saturation, and it does not, therefore, present itself in the practice of cementation. But since ordinary cementation is not automatically limited (as follows from the experiments cited), it is necessary in practice, in order to obtain a predetermined result, to work under definite conditions (of composition of the cement, of temperature, etc.) determined, in each case, empirically.

And here Charpy calls attention to the fact that it is possible to imagine conditions in which the cementation is *automatically limited;* this happens, for example, when using gaseous cements whose decomposition products have the tendency to decarburize the metal. Such cements are carbon monoxide, cyanogen and the hydrocarbons.

Granted this, Charpy reports the results of his experiments on the cementation of a fine wire of iron by means of carbon monoxide, results and experiments already published a year before in the note which I reviewed in the preceding pages. (See p. 45.) On the basis of these experiments and of the considerations already developed, extended to cyanogen and to the hydrocarbons, whose gaseous decomposition products (nitrogen and hydrogen, respectively) act as decarburizers of the steel, he deduces that "the cementation may be executed in such a way that the quantity of carbon absorbed is regulated automatically, and this *by using as cementing substance a continuous current of a gaseous mixture containing definite proportions of* *either carbon monoxide and carbon dioxide, cyanogen and nitrogen or hydrocarbons and hydrogen.*"

We shall see later how the conception expressed in indefinite form in these sentences of Charpy is not susceptible of practical application; this, moreover, is easy to understand when we think of the enormous practical difficulty of adjusting the mixture of carbon monoxide and carbon dioxide in which, to obtain appreciable cementations at temperatures sufficiently high so that the process may go on with sufficient rapidity, the proportion of carbon dioxide must be below 1% and determined with an accuracy greater than one part in a thousand.

We shall also see, however, how, taking into account the various elements (such as the distribution of the carbon in the cemented zones, the relation between the velocity of penetration of the carbon monoxide and of the carbon dioxide into the iron, the velocity of the reactions which take place in the process of cementation, the conditions of equilibrium between the gases in the cementing atmosphere and in the mass of the steel, etc.) which Charpy could not consider in his experiments,[1] it is in reality possible to obtain in practice the result whose possibility Charpy foresaw. But, I repeat, this result can be obtained under conditions of *industrial feasibility* only by means quite different from those suggested by Charpy, based on the use of gaseous mixtures in definite proportions. Of such means we shall treat later; for the present I only wish to point out how Charpy's preconceptions relative to the use of hydrocarbons to "limit" the cementation do not seem confirmed by more recent experiments.

Charpy's memoir concludes with some interesting observations on the action of carbon monoxide on manganese and on chromium. These metals, and especially chromium, when subjected to the action of carbon monoxide, absorb its oxygen, being transformed into mixtures of their oxides and of free carbon. Chromium preserves this property even when it is alloyed with other metals; for example, in chrome steels. "When a chrome steel is subjected to the action of carbon monoxide, a certain cementation occurs, but at the same time an oxidation also manifests itself. This, however, seems to be limited to the chromium, and does not proceed beyond the surface zone, because the oxide of chromium formed does not diffuse into the metal." We shall have occasion to see later how these facts can be clearly explained on the basis of the results of a series of most interesting investigations by

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[1] This is due, above all, to the fact that Charpy almost always used in his cementation experiments (except in a few cases) the iron in the form of wires or filings, in which it is evidently impossible to take into account the distribution of the carbon.

From the considerations which I shall have occasion to develop later, it will appear clear that the investigations of Charpy, carried out with the ability and acumen which distinguish the author, would certainly have led to the most interesting results (especially from the practical point of view) if the author had placed himself under such experimental conditions as to have been able to study the *distribution* of the carbon in the cemented zones.

Schenck, and how these investigations make it possible to determine with precision the course of the reactions which take place between carbon monoxide and the various metals.

Following the chronological order, we find a work of J. Lecarme, published in 1905 by the *Revue de Métallurgie*.[1] Although the contents of this work do not bear strictly on the process of carburization of cemented zones, but rather on the transformations which take place in the "heart" of the cemented pieces (to which, at least apparently, the carburization does not extend), yet the conclusions to which they lead, if the experimental facts on which they are based should ever receive more certain confirmation, would be of great importance for the study of cementation, as well from the theoretical as from the technical point of view.

Lecarme reports the results of several series of comparative bending tests, made on various samples of the same steel, some of which had been cemented and quenched under definite conditions while others had been subjected in a neutral medium or in the presence of substances capable of impeding the cementation (substances which Lecarme calls "anti-cements," keeping their composition secret), to the same thermal treatment to which the cemented specimens had been subjected.

From the brittleness of the cemented pieces, which was always greater than that of the others, Lecarme believes he can conclude:

1. "That the brittleness of the cemented soft steels is not due to the heating which accompanies the cementation;

2. "That the surface carbon cementation is accompanied by a chemical transformation of the center of the metal, which appears homogeneous throughout its whole mass. The new metal thus produced, when treated by the ordinary methods, that is, simply quenched at about 800° C., becomes brittle."

Lecarme adds that "with thermal treatment executed under suitable conditions, it is possible to suppress, in part, the brittleness of cemented soft steels without harm to the hardness of the surface layer," but concerning such useful treatment he furnishes no precise information.

The practical importance which these results would have, if they were ever confirmed, is evident. As to their theoretical importance, the fact of a chemical transformation *due exclusively to cementation* and manifesting itself in the metal lying *below the carburized* zone would show beyond doubt the marked intervention of gases in the process of cementation, or, at least, would be a proof that the process of cementation does not consist simply, as was supposed by Margueritte and later by Ledebur, in a process of solution of the solid carbon in the iron.

In a note immediately following Lecarme's work, Le Chatelier points out that the conclusions of that work are very interesting but that they are "not based on any precise experimental proof." Le Chatelier insists above all on the fact that in the bending tests on the cemented bars "the fracture of the cemented zone produces a crack, equivalent to a very sharp cut, the presence of which is sufficient to cause the breaking, through brittleness, of the greater part of soft steels. It would have been necessary, therefore, in order to obtain comparable results, to carry out the comparative tests on non-cemented bars after having made in them a cut as sharp as possible," which Lecarme did not do.

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[1] J. Lecarme, *Sur la fragilité des aciers doux cémentés* (*Revue de Métallurgie*, 1905, Vol. XI; *Mémoires*, pp. 516–525).

Le Chatelier adds that "it must, however, be acknowledged that Braune's experiments on the harmful influence of nitrogen lend a certain probability to the facts announced by Lecarme, *for in the usual processes of cementation the nitrogen is the carrying agent of the carbon.*"

As to the possibility, alluded to by Lecarme, of regenerating steel made brittle by cementation, Le Chatelier says he long since pointed out to various works a process capable of producing such an effect. We shall treat of this later.

Answering briefly Le Chatelier's observations,[1] Lecarme admits their justice but adds that he has been able to establish by means of a series of experiments that the difference in brittleness between the cemented bars and those simply heated persists, though to a less marked degree, even when the bending tests are executed on specimens obtained by removing, with an emery wheel, the brittle carburized zone. The later data reported by Lecarme are, however, absolutely insufficient to establish either the importance or even the reality of the phenomena. Precise investigations on this line would certainly be of great use.

On January 15, 1906, appeared an article by Ledebur,[2] in which the celebrated German metallurgist harshly criticises the work (reviewed a few pages back[3]) published two years before by Guillet in the *Mémoires de la Société des Ingénieurs Civils de France.*

Ledebur states that he has not read Guillet's work in the original text and that in his criticism he refers to the review of that article published about a year and a half before in *Stahl und Eisen.* He then explains the delay in the appearance of his criticisms by a long illness which he has suffered in the meantime and by the long time required by investigations on an industrial scale, which he has thought necessary to make as a basis for his objections, not considering as sufficient experiments carried out in the laboratory on a small scale.

The very full review of Guillet's work to which Ledebur refers[4] is compiled by Bauer, who reports the data and arguments contained in Guillet's memoir with great precision and in an entirely impersonal manner. The compiler allows himself, however, to set forth here and there some of his personal views, which he always takes care to distinguish clearly from Guillet's, and it must be admitted that many of his observations are justified. Such, for example, is the just criticism by Bauer of a statement of Guillet (which I have quoted, in italics, on p. 53) to the effect that in manganese cemented steels we pass, proceeding from the surface toward the interior, from a troostite layer to one of martensite and from this to a pearlitic one; it is, in fact, difficult to explain how this can happen when we remember the fact that troostite constitutes one of the end points of the passage of martensite to pearlite.

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[1] *Revue de Métallurgie,* 1905, pp. 720–721.

[2] *Stahl und Eisen,* 1906, Vol. XXVI, pp. 72–75.

[3] See p. 46 *et seq.*

[4] *Stahl und Eisen,* Sept., 1904, pp. 1058–1064.

Ledebur begins by upbraiding Guillet for having made use only of metallography and not of chemical analysis when studying the course of a process essentially chemical, such as that of the diffusion of carbon into iron. Then, against the conclusion of Guillet that the velocity of cementation is independent of the carbon content of the steel subjected to cementation, he cites the experiments of Saniter (which I have already briefly reviewed) which, on the basis of chemical analyses, showed that the velocity of cementation *diminishes* as the concentration of the carbon increases in the steel.

Ledebur denies, then, any scientific value whatever to the second series of Guillet's experiments, relative to the influence of time on the depth of cementation, since the results of those experiments are irregular, uncertain and, moreover, inconsistent with those obtained by other experimenters; for example, with those of Mannesmann.[1]

As to the third series of Guillet's investigations, relative to the influence of temperature on the course of cementation, Ledebur admits that they present marked interest. In fact, the earlier experiments of Arnold and MacWilliam,[2] which had already proved that below 750° C. the migration of carbon into iron does not take place, and that the velocity of this migration increases with rise in temperature, related to the passage of the carbon from a mass of steel in which its concentration was high to another in which it was low, rather than to the true process of cementation, properly so called. On the other hand, in the researches of Mannesmann,[3] which had proved that the cementation is more rapid the higher the temperature, the measurements of the temperature were certainly inexact.

But there is one point on which Ledebur declares himself to be of an opinion entirely contrary to that of Guillet; this relates to the "mechanism" of the process of cementation. In fact, Ledebur maintains that, on the basis of the

[1] These results of Mannesmann are briefly summarized in the first chapter of this book (see p. 19 and especially the figure).

[2] See pp. 34–37.

[3] See p. 14 *et seq.*

exceedingly numerous and conclusive experiments of many able experimenters—among whom he cites Margueritte, Roberts-Austen, Hempel and Mannesmann (whose experiments are already summarized in preceding chapters)—it is now absurd to admit the theory of Caron and Guillet that cementation can not be effected directly by the action of solid carbon but is always produced by cyanides formed by the action of the nitrogen of the air on the alkalis contained in the ashes of the wood charcoal used as cement.

Ledebur censures Guillet for having carried out the experiments to prove his assertion only in the laboratory, on a small scale,[1] continuing the duration of the cementations only up to eight hours and limiting himself to measuring the depths of the cemented layers without determining, by chemical means, their carbon content. He proposes to show, by means of experiments carried out on an industrial scale, that the cementation is effected by the direct action of the solid carbon placed in contact with the iron, independently of the intervention of volatile carburizing substances.

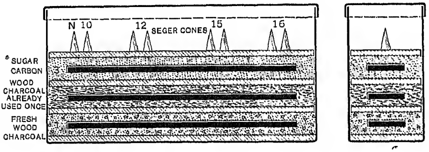

FIG. 17.

Ledebur's first group of two comparative experiments, carried out by cementing Lancanshire iron in closed graphite crucibles, using as cements wood charcoal and sugar carbon, did not give clear-cut results because even the sugar carbon contained considerable quantities of ash, quite rich in alkali.

A new series of three experiments was carried out in the "Bergische Stahlindustrie" foundry of Remscheid, by cementing bars of Lancanshire iron, 35 cm. long, 8 cm. wide and 1.5 cm. thick. The iron bars were placed in a well-closed sheet-iron box in the manner indicated in the accompanying figure (see Fig. 17), surrounding each one with a cement and separating with refractory bricks the spaces occupied by the individual cements. The cement filling the lower space was "new" powdered wood charcoal; the intermediate chamber contained wood charcoal already used once as cement; finally, the cement used for the upper chamber was sugar carbon, previously washed with acids. In the free space remaining in the upper part of the sheet-iron box were placed Seger cones, corresponding to temperatures of 950°, 890°, 800° and 770° C.

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[1] I shall have occasion to bring out later how unjustified is this reproof of Guillet by Ledebur.

The box remained in the furnace during 408 hours of firing. When removed from the fire, three of the Seger cones had melted completely, while the fourth, corresponding to 950°, had merely suffered a slight softening; the maximum temperature reached by the box was therefore 950°.

The analyses of the bars and of the cements gave the following results:

Lancashire iron, before cementation	0.144% of carbon
The same, cemented with "new" wood charcoal	1.45% of carbon
The same, cemented with used wood charcoal	1.23% of carbon
The same, cemented with sugar carbon	1.38% of carbon
Percentage of ashes (as residue in the combustion):	
"New" wood charcoal	2.00%
Used wood charcoal	10.75%
Sugar carbon	0.75%

The ashes of the sugar carbon were almost completely free from alkali and consisted of almost pure iron oxide. Nevertheless, the carburizing action of the sugar carbon was almost equal to that of the "new" wood charcoal and higher than that of the wood charcoal already used. These experiments show anew that for the cementation of iron the intervention of gaseous carburizing compounds is in no wise necessary and that, instead, the carbon can penetrate directly into the iron and diffuse into it until it reaches a limit of saturation depending upon the temperature.

This does not mean, naturally, that carburizing gases or vapors, and especially hydrocarbons and cyanides, do not cement iron *even more rapidly;* this is a fact known for a long time and applied in industry for superficial cementation and, more recently, in the manufacture of armor for ships.

Ledebur then observes that, at least in the form in which the author expresses himself, the assertion of Guillet that "the use of too high a temperature in the cementation may give rise to a decarburization of the iron" is inexact; in fact, Ledebur remarks justly that all the experiments show with the greatest certainty that cementation carried out at too high a temperature can produce only an excessive carburization of the iron, and that the decarburization can manifest itself only as the result of the exhaustion of the cement and of consequent access of air to contact with the metal.

Ledebur concludes with some considerations on the probable causes of the known phenomenon of the decrease in the efficiency of cements with use. He does not consider as correct the explanation of the phenomenon advanced by Margueritte and by Mannesmann, who attribute it to the increase in "compactness" or in "density" which manifests itself in the particles of wood charcoal subjected to a long heating. If this were so, it should be possible to distinguish with the microscope "new" carbon from that already used, which, however, he has never succeeded in doing. Moreover, contrary to the hypothesis of Margueritte is the fact, shown by experiment, that various very dense carbons cement iron more intensely than others which are considerably lighter. Ledebur holds, rather, that the cause of the phenomenon lies in the ashes, the proportion of which in the carbon increases (as the experiments cited by the author, and others, show) with use of the latter, and this for two reasons; the first is that in every cementation a little of the carbon burns up on account of the air occluded in it; the second is the fact that during the various operations a little sand, coming, especially, from the cover of the boxes, becomes mixed with the powdered carbon. So that, first, the quantity of efficient carbon is diminished by the presence of these foreign substances, and, in the second place, the basic components of the ashes of the carbon and the siliceous sand fallen into it form a mass fusible at the temperature of the cementation, which covers the grains of carbon, diminishing their contact with the iron.

A lengthy summary of Ledebur's memoir was published a few months later by the *Revue de Métallurgie*[1] and followed, in the same number of the French Review, by a brief reply by Guillet,[2] who answers successively the three principal criticisms directed against him by Ledebur, as follows:

1. To the criticism of having determined the course of the cementation by means of microscopical examination instead of by chemical analyses, Guillet answers that Ledebur would not have made that criticism if, instead of the summary of his work published by *Stahl und Eisen*, he had read his original memoir.

Now, leaving aside the consideration that even in the summary of *Stahl und Eisen* mention is made, *as in the original memoir*, of gravimetric determinations of the carbon *in the surface layers* of the cemented pieces and that, therefore, Ledebur's opinion would not have been modified by reading the original memoir, Guillet's statement that he can not see what interest the use of chemical analysis can present in determining *the velocity of penetration of the carbon* seems somewhat immoderate. In fact, we shall see later how analyses of the successive layers of the cemented zones furnish most interesting data on the mechanical properties of the cemented pieces, due to the "distribution" of the carbon in these zones. Moreover, the observation of Ledebur assumes the very greatest importance as regards the cementation of special steels, for which, as we shall see later on the basis of practical examples, the measure of the depth of cementation made by means of microscopical examination furnishes, in the majority of cases, but uncertain and inexact data.

2. As to the experiments of Saniter cited by Ledebur, Guillet observes very justly that they do not at all contradict his own; he, in fact, determined the *velocity of penetration* of the carbon, finding it constant for steels containing from 0 to 0.5% of carbon, while Saniter had shown that the velocity with

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[1] *Mémoires*, 1906, pp. 222–226.

[2] *Mémoires*, 1906, pp. 227–228.

which the *concentration* of the carbon increases as the result of cementation diminishes when this concentration has reached the value 1.64%.

And here, to this correct observation of Guillet, it may be added that Saniter, working on fine iron wires, could certainly not determine the "depth" of cementation and, therefore, neither the "velocity of cementation" in the sense in which this datum is meant in Guillet's experiments.

3. Guillet holds that the only interesting criticism advanced against him by Ledebur is that regarding the way of considering the course of the cementation.

While Ledebur maintains that carbon is the agent of the cementation, Guillet "believes that he has shown that the active agent in every industrial cementation *is a cyanide or a carbide.* He insists, however, that carbon alone does not cement."

As to the experiments of Margueritte, of Roberts-Austen, etc., Guillet holds that cementation experiments carried out with diamonds in a current of hydrogen[1] prove nothing, since hydrogen is not the desired inactive medium. As to the assertions of several authors that in various experiments, carried out under definite conditions, cementation had manifested itself only at the points where the carbon was in contact with the iron, Guillet wonders if it is "possible to verify such facts." But we shall see further on how he himself later had occasion to state such facts.

Guillet adds here the results of two other experiments. In the first, carried out by heating sugar carbon in contact with iron for twenty-four hours in a vacuum, not the least cementation detectable by the microscope or by chemical analysis manifested itself. In the second "industrial" experiment, carried out by cementing iron for 300 hours at 1000° C. in sugar carbon, there was formed only a carburized layer 2/10 mm. thick, which Guillet attributes to the action of small quantities of ashes. Under the same conditions the mixture of wood charcoal and barium carbonate gave a "penetration" of 20 mm.—Guillet finally affirms—and in this (as we shall see) he is evidently reasonable—that Ledebur's experiments do not certainly prove that carbon by itself can cement.

He supports his assertion by the fact that in the majority of cases the carbon used by Ledebur contained quantities of ashes sufficient to explain the cementation by the intervention of cyanides, and in the single experiment in which the ashes of the sugar carbon consisted solely of almost pure iron oxide, he admits that the vessels might have yielded substances (and especially alkaline bases) useful in the cementation. We shall see later, however, that the lack of proof by Ledebur's experiments lies in causes quite different from those just indicated.

Guillet then invites Ledebur to prove the exactness of his theory by making a prolonged cementation *in a vacuum* in the presence of sugar carbon perfectly purified by preliminary treatment with chlorine at red heat.

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[1] It is well to note that some of the cementations of Roberts-Austen were carried out *in a vacuum.*

4. Guillet does not know in what part of his memoir Ledebur found the phrase, which we saw criticised by him, the text of which (according to Ledebur) is: "too high a temperature, *in the process of surface hardening*, gives rise to a decarburization of the iron."

Now, in truth, the text of Guillet's work (here, as in all other points, faithfully reported in the summary of *Stahl und Eisen*) does not contain exactly the phrase given by Ledebur. In fact, it is in speaking of the effects of heating *in general* that Guillet says that "if the temperature is too high, a decarburization of the metal may manifest itself." But since this phrase forms part of the views of Guillet on the disadvantages which the use of too high temperatures may produce in cementation, considerations which led Guillet to conclude that it is necessary to cement at the lowest possible temperature, it was natural enough that Ledebur should consider that the observations of Guillet referred to the heating which accompanies the cementation. At any rate it would have been useful if, in his answer, Guillet had cleared up better the mistake due merely to the inexact interpretation of his sentence.

In one of the first pages (p. 154) of the same number of the *Revue de Métallurgie*, the Editor makes some observations on the polemic which had arisen between Guillet and Ledebur regarding cementation. These observations, which, from their clearness and the breadth of the views which they contain, are certainly due to the pen of Le Chatelier, are worth noting here.

The Editor holds that the disagreement between Ledebur and Guillet is due in great part to the fact that the former means to indicate by the word *cementation* the process for the manufacture of steel founded on the total carburization of relatively thick bars of iron heated for very long times in contact with carburizing substances, while the latter deals only with surface cementation, limited to the formation of carburized layers of small thickness (1 or 2 mm.). It is evident, in fact, that the difference of these two points of view results in the two experimenters giving a totally different signification to the expression "velocity of cementation"; while to Ledebur this velocity refers to the increase in *concentration* of the carbon, to Guillet it refers to the *depth* to which the carbon penetrates.

The Editor adds, that "notwithstanding the quite widely prevalent contrary opinion, it is very difficult, not to say impossible, to admit that the cementing action of carbon monoxide is *nil*. *It must be extremely slow*, as its dissociation into carbon and carbon dioxide is arrested as soon as the smallest trace of this latter gas is produced; this must again be reduced in contact with carbon in order that the operation may begin again."

Le Chatelier, holds, then, that it may be admitted as certain:

1. "That many gaseous substances permit the rapid transport of carbon to the iron, without direct contact of the two substances.

2. "That the diffusion of carbon placed in intimate contact with iron is likewise possible. The disappearance of temper-carbon on heating is the proof of it."

And he concludes:

"The only point on which there can be any discussion is as to whether, in practice, this second method of penetration of carbon into iron takes place in the industrial processes of cementation. The experiments of Ledebur are not sufficient to prove it, as it would have been necessary to work in an absolute vacuum and with materials freed from the last traces of alkalis, such as with carbon first heated to white heat in a current of chlorine." We shall see later how these last observations contain exactly the key to the problem.

We wish to point out now, however, that the causes of disagreement between the conclusions of Guillet and those of Ledebur can be understood better if it is observed that, while the former experimenter proposed to determine the course of the process of carburization of solid iron by effecting it under the simplest and most rigorously defined conditions, and by considering it as a chemical process capable of a theoretical explanation, Ledebur sought, instead, to establish in what way the process takes place under the conditions of industrial practice. But Guillet's hypothesis, founded on the intervention of gases, is precisely that which applies (suitably modified) in the process of industrial cementation, while the explanation accepted by Ledebur does not hold, therein, except to a very small degree. Ledebur's hypothesis, in fact, enters into play to a marked extent only in cases in which the experiments are carried out under rigorously defined experimental conditions analogous to those adopted by Guillet.

Later the journal *Metallurgie* published a paper by R. Bruch[1] in which the author undertakes the accurate study of the course of cementation carried out with gaseous cements. The experiments are carried out under well-defined conditions, using carefully dried gases and cementing cylinders of steel 10 mm. in diameter, placed in tubes of glazed procelain kept at constant temperatures determined with a Le Chatelier pyrometer, and using a tubular electric furnace with platinum ribbon, made by Heraeus. Moreover, the author determined the carbon by chemical analysis of five successive layers (each $\frac{1}{2}$ mm. thick) turned on the lathe from the cylinders of cemented steel, and subjected his specimens to an accurate microscopical examination. The gases used were: the illuminating gas of the city of Aachen, petroleum vapor, acetylene, and pure carbon monoxide. The iron subjected to the cementation was a very pure, extra soft iron (with 0.03% of carbon).

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[1] *Ueber Zementierversuche mit gas-, resp. dampfförmigen Zementiermitteln* (*Métallurgie*, 1906, Vol. III, pp. 123–128).

The experimental conditions were therefore very good, and could easily have led Bruch to draw most interesting conclusions regarding the process of cementation if he had subjected the results of his experiments to a rational study. However, he makes use of his numerous carbon determinations, made on the successive layers of the cemented cylinders, only to study how the velocity of penetration of the carbon varies with variations in the temperature. He thus merely reaches the conclusion, not at all new, that this velocity increases with increase in temperature; we shall see later that the results of these analyses could have led to valuable conclusions if he had made use of them (confirming them by a more exact metallographical examination) to determine the *distribution* of the carbon in the various cemented zones.

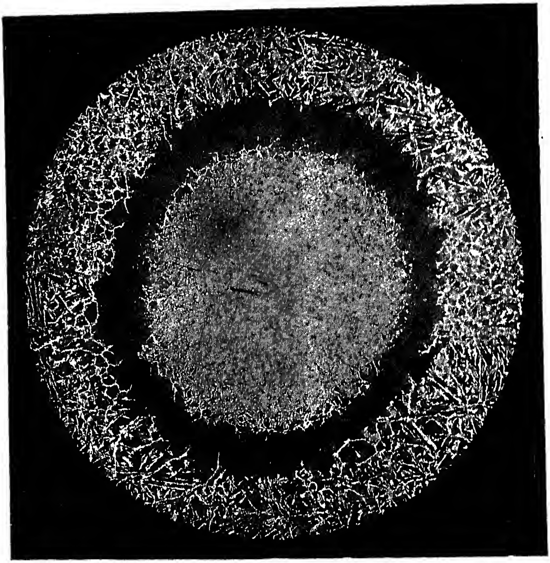

FIG. 18.

Besides the conclusion mentioned, Bruch also concludes that gases cement iron at temperatures below 700° C.

However, besides these two observations, Bruch makes two others which would certainly be more important if they were not evidently erroneous. The first refers to the cementing action of carbon monoxide, an action which Bruch holds is absolutely *nil.* We shall see later that Bruch was wrong, also the probable explanation of his error.

The second erroneous observation of Bruch refers to the way in which the concentration of the carbon varies in the successive layers of the cemented zones. Bruch maintains that the microscopic examination of his cemented specimens confirms the hypothesis that cementation consists in a process of "diffusion" or of "*solution*" of the carbon, for it shows that in these specimens there is "a *continuous and uniform* increase in the carbon content as we pass from the nucleus to the periphery."

It is sufficient to examine Fig. 18 to become convinced that the conclusions which can be drawn from the examination of Bruch's cemented specimens are quite different from those drawn by Bruch himself. This is but the reproduction of the microphotograph contained in Bruch's work to which Bruch refers to confirm his assertion. In this photograph (which reproduces, enlargement 10 diameters, the polished and etched section of a soft steel cylinder cemented by acetylene gas at 1050° C. for seven hours) is clearly seen the sudden transition from the external hyper-eutectic zone, rich in cementite, to the intermediate eutectic zone, formed of pure pearlite; and from this to the hypo-eutetic nucleus.

Moreover, since it is certain (and the micrograph and the analyses ot Bruch prove it) that the carbon content increases from the center to the periphery of the steel cylinder, and it is no less certain that this content is constant (and equal to 0.9%) in the whole dark zone formed of pure pearlite, it is evidently absurd to say that the concentration of the carbon increases "in a continuous and uniform way" from the nucleus to the periphery.

We shall see later that these discontinuities are not due to the cementation but to phenomena following it. So that, if the proof offered by Bruch has no value, the hypothesis, independently of it, might nevertheless be correct. With this we shall have occasion to deal later, basing our remarks on more precise experimental data.

We may cite a work on the same line, published in the same year (1906), by Partiot in the *Revue de Métallurgie.*[1] This, while contributing no new facts, contains some clear observations on the preceding investigations. Thus the author, subjecting to a brief critical examination the experiments on which Guillet and Ledebur had based their conclusions, points out how these two experimenters had not taken into account two important data, the influence of which was especially strong in the experiments of Ledebur, carried out by heating large masses during very long intervals of time. These data are: the time necessary to reach the constant temperature of cementation, and the "exhaustion" of the cements used.

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[1] Partiot, *Sur quelques points obscurs de la théorie de la cémentation. Revue de Métallurgie*, 1906, pp. 535–540.

The paper of Partiot then contains remarks on the need of carrying out experimental investigations on the substances which he, like others before, calls "anti-cements," *i.e.*, those capable of impeding the carburization of definite zones of steel objects subjected to cementation, and on the phenomena of brittleness and deformation which manifest themselves in pieces subjected to cementation.

Among the investigations on the cementation of steel published during the following year (1907), we must mention a work of Braune, which appeared in the *Bihang till Jernkontorets Annaler;*[1] a summary of this (to which alone I can refer) is published in *Stahl und Eisen.*[2]

The interesting researches of Braune on the influence of the nitrogen contained in steel on its mechanical properties are well known.

In the memoir with which we are now dealing, he reports the results of a series of investigations on the absorption of nitrogen by iron subjected to cementation, and on the effect of this absorption on the mechanical properties of the cemented steel.

A series of cementations, carried out under various conditions of temperature and of time, with various cements (wood charcoal, animal charcoal, etc.), revealed an absorption of nitrogen by the steel subjected to cementation, in amounts varying with the conditions under which the cementation is effected and with variations in the nature of the cement used.

Braune's experiments do not yet seem, however, to indicate with accuracy the relations which exist between the phenomenon of nitrogen absorption and the special mechanical properties acquired by the steel subjected to cementation.

Two memoirs on the surface cementation of steel were presented at the meeting of the Iron and Steel Institute[3] held in Vienna in September of the same year (1907).

The first, by C. Shaw Scott, does not contain new experimental data worthy of note. In it the author repeats (for example, on the intervention of nitrogen in the process of cementation) many of the observations and remarks made by other experimenters and contained in the publications summarized in the preceding pages. Further, his experiments can give no exact information, since they were carried out with a cement (carbonized leather) of very indefinite chemical composition.

[1] 1907, No. 3, pp. 191–204.

[2] 1907, pp. 1395–1398.

[3] *Journal of the Iron and Steel Institute*, 1907, pp. 120–136.

The second memoir is by C. O. Bannister and W. J. Lambert.[1] This contains the results of a series of cementation tests made with a cement designated by the name of "Red Scintilla," but the composition of which is not given. The authors report also, but not very clearly, the results of the micrographic examination made both on cemented and quenched specimens of steel, and on specimens cemented and allowed to cool slowly. These last observations are a repetition of those of Bruch, which I have already summarized and commented upon.[2]

The micrographic observations on the cemented and hardened specimens led the authors to considerations of very doubtful value on the relations existing between the areas occupied by the pearlite before and by the martensite after the hardening.

The authors also made measurements of the depth of cementation, but for this (if we except one case in which they made four carbon determinations), instead of making use of microscopic examination and chemical analysis, they preferred to use the file, attempting to determine with this the hardness of the successive layers of the cemented cylinders exposed by removing, by means of an emery wheel, definite quantities of steel in coaxial cylindrical zones. We shall see later (in the second part of this volume) how inexact may be the results obtained in such a way.

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[1] *Journal of the Iron and Steel Institute*, 1907, pp. 114–119.

[2] See p. 65 *et seq.*

CHAPTER IV

THE LATEST STUDIES ON THE PROCESS OF CEMENTATION

I have already given at the beginning of the preceding chapter the reasons which led to concluding with 1907 a period, clearly distinct from the others, of scientific investigations on the process of the cementation of steel.

We will now review the work done since 1907.

Having had occasion to carry out myself during 1905–1907 a long series of experimental studies on the industrial application on a large scale of the processes of cementation,[1] I very soon realized that the scientific fundamentals of these processes as then known were anything but certain and complete, so that after having for some years prosecuted my industrial investigations I saw the necessity of taking up again the scientific study of cementation; this I have been able to do with the kind collaboration of various other persons.

Since these studies, the results of which I began to publish in the summer of 1908, have made it possible to clear up various interesting points of the theory of cementation and have furnished a useful guide for the industrial application of the processes of cementation, I will give here the results of my investigations, together with the researches contemporaneously carried out by others. A part of my investigations have recently been summarized by Portevin in the *Revue de Métallurgie.*

The first publication[2] contains only a small part of the results of the investigations carried out on a large scale in the works, chosen from among the few which I am allowed to publish, with the essential object of pointing out how it is possible in practice to produce a variation of the *distribution* of the carbon in the cemented zones, not only by using cements of definite nature but also by simply varying the conditions under which the cementation is effected. In these is systematically taken into account the *distribution* of the carbon in the cemented zones, by determining analytically the carbon in *a series* of successive layers of these zones. The data of such analyses, reproduced in a "concentration-depth" diagram (by representing on the axis of abscissas the distance of the median surface of the analyzed layer from the external surface of the cemented specimen of steel and as ordinates the carbon contents obtained from the corresponding analyses), furnish a clear diagram of the "distribution" of the carbon in the cemented zone, and we shall see how this information can lead to interesting theoretical and practical results.

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[1] Of these studies, carried out in great part at foreign industrial establishments, I can report (for reasons easy to understand) almost nothing.

[2] F. Giolitti, *Ricerche sulla fabbricazione dell'acciaio cementato*, Note I: *Gazzetta Chimica Italiana*, 1908, Vol. XXXVIII, Part II.

A first series of experiments, intended to furnish reference data on the "velocities of penetration" of the carbon which can be obtained with the processes usually employed in industrial practice, were carried out by cementing at various temperatures, under the conditions usually adopted in industrial establishements, bars of soft Martin-Siemens steel in the form of parallelepipedons 40 × 40 × 200 mm. There was used as cement one of the mixtures most frequently employed in practice, consisting of ground wood charcoal treated with 5% of potassium ferrocyanide and mixed with an equal weight of dry barium carbonate. The results obtained are reported in the table reproduced herewith and represented graphically in the diagram reproduced in Fig. 19. In the diagram, ordinates correspond to the depths of cementation, in millimeters, measured on sections of the bars from the edge to the point at which the cementation of the carbon is reduced to 0.2%, while abscissas represent the duration of the cementation, in hours.

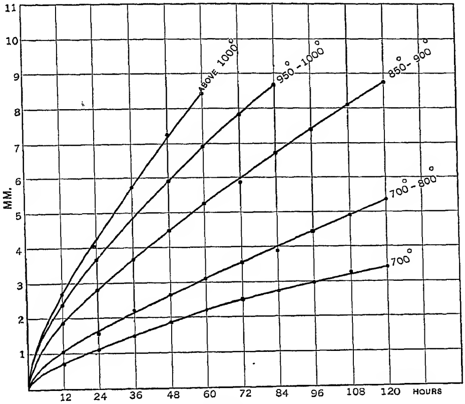

FIG. 19.

The results obtained, aside from their evident practical interest, serve as useful terms of comparison for later experiments carried out with cements of various natures. I shall omit, for the present, the theories to which these first results have given rise, since the later experiments furnish more precise and interesting data.

Length of the cementation in hours	Depths in millimeters of the cemented zones at the following tempeatures				
	About 700°	750°–780°	850°–900°	950°–1000°	Above 1000°
12	0.75	1.10	1.95	2.45	2.65
24	1.15	1.60	2.85	3.70	4.00
36	1.50	2.25	3.65	5.10	5.80
48	1.90	2.80	4.50	5.90	7.30
60	2.20	3.15	5.30	7.00	8.45
72	2.55	3.60	5.90	7.80	....
84	2.80	3.95	6.75	8.70	....
96	3.00	4.50	7.45	....	....
108	3.30	4.95	8.10	....	....
120	3.45	5.45	8.75	....	....

In the same note, these first experiments are followed by others, showing the *distribution* of the carbon in the cemented zones. The cement used in this second series of experiments was a mixture containing 70% of wood charcoal and 30% of animal charcoal. The steel was in the form of cylindrical bars or rectangular parallelepipedons, and had the following composition:

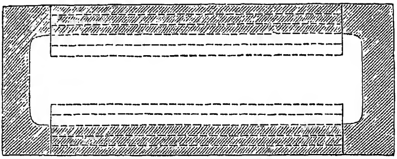

FIG. 20.

Carbon	0.05 percent.
Manganese	0.28 percent.
Silicon	0.011 percent.
Phosphorus	0.035 percent.
Sulphur	0.042 percent.

Successive layers 1 mm. thick were removed from the slowly cooled cemented bars (on the lathe or on the planer, according as they were cylinders or parallelepipedons), taking care to leave intact the portions near the angles of the specimens. Fig. 20 shows schematically the method followed in removing the successive layers; in it the shaded surface represents the section of the carburized zone, while dotted lines bound the sections of the successive layers removed on the lathe or on the planer.

A series of seven cementations, followed by analysis of successive layers, 1 mm. thick, of the cemented bars, gave the results reported in the following tables:

I

Length of the cementation, 36 hours. Temperature, 850°–880° C.

Depth in mm.	Carbon, percent.	Depth in mm.	Carbon, percent.
0.5	1.02	6.5	0.16
1.5	1.00	7.5	0.14
2.5	0.94	8.5	0.12
3.5	0.66	9.5	0.10
4.5	0.43	10.5	0.08
5.5	0.22	11.5	0.07

II

Length of cementation, 60 hours. Temperature, 850°–880°

Depth in mm.	Carbon, percent.	Depth in mm.	Carbon, percent.
0.5	1.03	7.5	0.33
1.5	1.02	8.5	0.24
2.5	1.00	9.5	0.18
3.5	0.95	10.5	0.14
4.5	0.83	11.5	0.11
5.5	0.66	12.5	0.09
6.5	0.50	13.5	0.08

III

Length of cementation, 96 hours. Temperature, 850°–880°

Depth in mm.	Carbon, percent.	Depth in mm.	Carbon, percent.
0.5	1.04	9.5	0.42
1.5	1.03	10.5	0.33
3.5	0.99	11.5	0.27
4.5	0.92	12.5	0.23
5.5	0.84	14.5	0.16
6.5	0.73	15.5	0.14
8.5	0.53	17.5	0.11

IV

Length of cementation, 360 hours. Temperature, 850°–880°

Depth in mm.	Carbon, percent.	Depth in mm.	Carbon, percent.
0.5	1.01	22.5	0.43
2.5	0.95	24.5	0.37
4.5	0.90	26.5	0.33
6.5	0.85	28.5	0.28
8.5	0.79	30.5	0.25
10.5	0.73	32.5	0.22
12.5	0.67	34.5	0.18
14.5	0.62	36.5	0.17
16.5	0.57	38.5	0.15
18.5	0.52	40.5	0.14
20.5	0.47	....	....

V

Length of cementation, 24 hours. Temperature, 1050°

Depth in mm.	Carbon, percent.	Depth in mm.	Carbon, percent.
0.5	0.72	6.5	0.29
2.5	0.58	9.6	0.17
4.5	0.43	12.5	0.09

VI

Length of cementation, 36 hours. Temperature, 1050°

Depth in mm.	Carbon, percent.	Depth in mm.	Carbon, percent.
0.5	0.84	10.5	0.27
4.5	0.55	14.5	0.18
7.5	0.39	17.5	0.14

VII

Length of cementation, 96 hours. Temperature, 1050°.

Depth in mm.	Carbon percent.	Depth in mm.	Carbon percent.
0.5	0.99	10.5	0.50
4.5	0.72	17.5	0.33

These numerical data are reproduced, in the manner which I have just indicated, in the seven "concentration-depth" diagrams in Fig. 21.

From these diagrams it is seen clearly how the temperature at which the cementation is effected and the length of the operation influence strongly the *form* of the curves which represent the *distribution* of the carbon in the cemented zones. I gave a very simple explanation of this phenomenon in the same note which I am now reviewing, but I prefer to speak of it somewhat later, when I shall treat of the results of other experiments, carried out under better defined conditions, which have furnished a surer confirmation of this explanation I shall then have occasion to refer to the tables and the diagrams which I have here reproduced.

It is well to keep in mind that the experiments which I have summarized were carried out on an industrial scale and the results can not, therefore, represent data as rigorously precise as those furnished by later experimental researches. Nevertheless, even taking into account only the "qualitative" significance, so to speak, of the experiments which I have summarized, we shall see later how the simple "form" of the curve which represents the *variation* in the concentration of the carbon in the various successive layers of the cemented zones has an influence on the mechanical properties of the cemented pieces at least equal to that of the total quantity of the carbon which has penetrated into the steel during the cementation and of the depth reached by this carbon.

Having thus established the fact that in industrial practice marked differences can manifest themselves in the distribution of the carbon in the cemented zones, I undertook a series of investigations in the laboratory, carried out under rigorously defined conditions, in order to learn the relations which exist between the results of the cementation (especially as regards the *variations* in the concentration of the carbon at the various points of the cemented zones) and the conditions under which the cementation is effected,

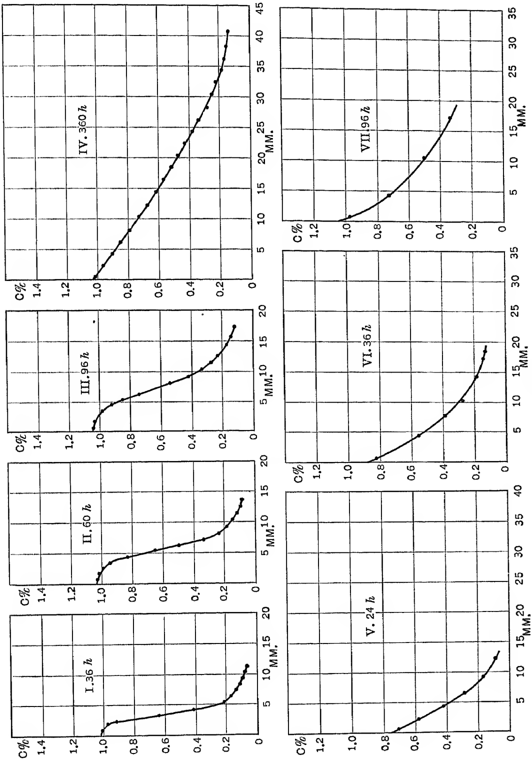

FIG. 21.

that is, the nature of the cement, the temperature, the pressure, and the thermal treatments which accompany and follow the cementation proper. I was thus able to discover the relations which exist between the distribution of the carbon in the carburized zone and the mechanical properties of the cemented pieces, so as to improve the latter by varying the former.

A first series of laboratory experiments, carried out and published in collaboration with Doctor Carnevali, had as its object to investigate the cementation of steels of low carbon content when working at various definite and constant temperatures, with carburizing gases of well-defined chemical nature, at pressures equal to or lower than atmospheric pressure.

The results of this series of investigations were collected into a paper published in the summer of 1908.[1]

The steel used, in the form of cylinders 10 mm. in diameter and 50 mm. long, had the following composition:

Carbon	0.06 percent.
Manganese	0.17 percent.
Silicon	0.01 percent.
Sulphur	0.04 percent.
Phosphorus	0.05 percent.

The pure gases used as cements were ethylene, methane, and carbon monoxide. Moreover, we made comparative experiments with the illuminating gas of the city of Rome, which then had the following composition:

Carbon dioxide	1.60 percent.
Hydrocarbons of the ethylene series (C_nH_{2n})	3.40 percent.
Oxygen	0.20 percent.
Carbon monoxide	10.80 percent.
Hydrogen	51.95 percent.
Methane	31.58 percent.
Nitrogen (by difference)	0.47 percent.

Fig. 22 represeents the apparatus by means of which it was possible to work under rigorously defined conditions. The gas displaced from the Mariotte bottle *I* (by means of water saturated with gas) and purified and dried in the bottles α, β, γ, δ, passed with definite and uniform velocity into contact with the cylinders of steel contained in the cementation chamber, the glazed porcelain tube *A*, 36 mm. in diameter, closed perfectly gas-tight, and heated to a constant and uniform temperature by means of a Heraeus electric furnace with platinum ribbon *E*. The temperature of the furnace and, therefore, of the cementation chamber could easily be kept exactly constant at the desired point by means of the rheostat *Q*, inserted in the electric circuit. The temperature was then measured (to an accuracy 2° C.) at various points of the cementation chamber by means of a galvanometer connected with a

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[1] F. Giolitti and F. Carnevali: *Ricerche sulla fabbricazione dell'acciaio cementato*, II; Cementazione di acciai a basso tenore di carbonio, coi gas alla pressione atmosferica e a pressione ridotta, *Gazz. Chimica Italiana*, 1908, Vol. XXXVIII, Part II, pp. 309–351.

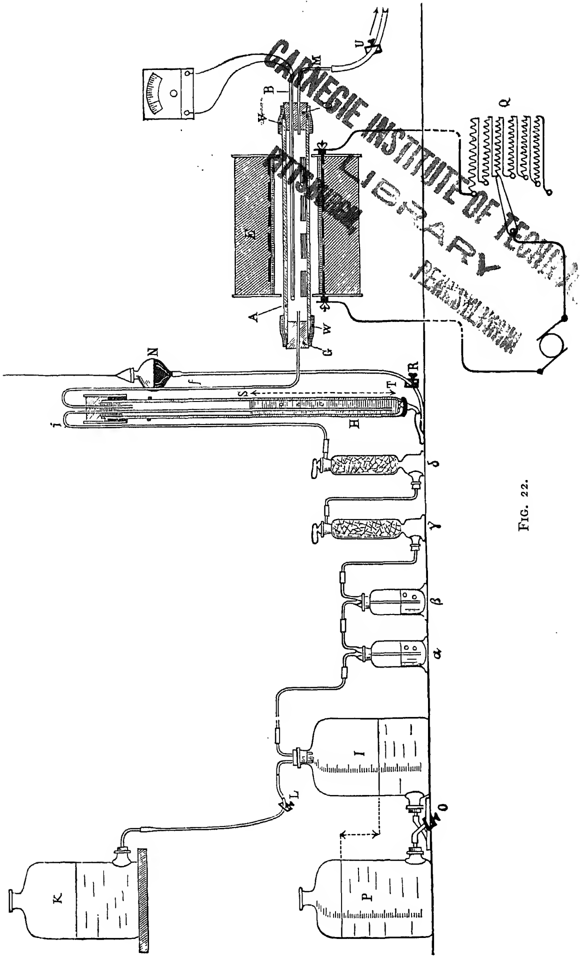

FIG. 22.

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Number	Carburizing gas used	Length of cementation (hours)	Pressure of carburizing gas (mm. mercury)	Temperature (degrees C.)	Volume of gas used (liters)	State of the surface of the steel cylinders after the cementation	Thickness of the	
								Thick-
							Total thickness (mm.)	Hyper-eutectic (mm.)
1	Carbon monoxide	6	761	810	10	No deposit of carbon...	0.1	.....
2	Washed and ignited wood charcoal..........	6⅔	761	820	..	No deposit of carbon...	0.1	.....
3	Wood charcoal and CO	6	761	810	6	No deposit of carbon...	0.25	.....
4	Wood charcoal first heated at 300° in CO.....	6	761	760	..	Deposit of brilliant hexagonal scales.........	.....	.....
5	Carbon monoxide	7	761	760	10	No deposit of carbon...	0.05	.....
6	Carbon monoxide	7	657	760	10	No deposit of carbon...	.....	.....
7	Carbon monoxide	7	568	770	10	No deposit of carbon...	.....	.....
8	Carbon monoxide	7	450	770	10	No deposit of carbon...	.....	.....
9	Wood charcoal and CO........	7	548	780	10	No deposit of carbon...	2	.....
10	Carbon monoxide	7	760	780	10	No deposit of carbon...	0.2	.....
11	Ethylene........	7	759	780	10	Deposit of very fine carbon in some parts of the cylinders.........	0.3	0.1
12	Ethylene........	7	454	780	7	Deposit of very fine carbon in some parts of the cylinders.........	0.3	0.1
13	Ethylene........	7	454	780	12	Deposit of very fine carbon in some parts of the cylinders.........	0.3	0.1
14	Methane........	7	759	780	8	Very small deposit of spongy carbon........	.....	.....
15	Methane........	7	453	780	8	Almost no deposit of carbon...............	.....	.....
16	Illuminating gas.	7	760	780	15	Small deposit of spongy carbon...............	.....	.....
17	Illuminating gas.	7	613	780	15	Small deposit of spongy carbon...............	.....	.....
18	Illuminating gas.	7	463	780	15	No deposit of carbon...	.....	.....
19	Ethylene........	5	760	900	7	Abundant deposit of finely divided carbon..	1.3	0.3
20	Ethylene........	5	609	900	7	Abundant deposit of finely divided carbon..	0.9	0.2
21	Ethylene........	5	458	900	7	Abundant deposit of finely divided carbon..	0.3	0.05
22	Carbon monoxide	5	760	900	7	No deposit of carbon...	1	0
23	Carbon monoxide	5	461	900	7	No deposit of carbon...	0.6	.....
24	Methane........	5	760	900	7	Abundant deposit of pulverulent carbon....	0.8	0.15

cemented zone		Distribution of the carbon in the cemented zone	Maximum concentration of carbon (cem. zone) percent.	Remarks
ness of the zone				
Eutectic (mm.)	Hypo-eutectic (mm.)			
....	0.1	According to Type I...	0.6	......
0.05	0.05	According to Type II..	0.9–1	Cementation takes place only at the points where the contact between the iron and the carbon is best.
0.01	0.15	According to Type II..	0.9–1	....
....	.....	....	.....	No cementation.
....	0.05	According to Type I...	.....	....
....	.....	....	.....	No cementation.
....	.....	....	.....	No cementation.
....	.....	....	.....	No cementation.
....	.....	....	.....	Very faint cementation, visible only with very great enlargement.
....	0.2	According to Type I...	.....	....
0.1	0.1	According to Type II. .	.....	The cementation is very faint and intermediate between Types I and II at the points where no carbon deposit has formed.
0.1	0.1	According to Type II. .	.....	The cementation is very faint and intermediate between Types I and II at the points where no carbon deposit has formed.
0.1	0.1	According to Type II. .	.....	The cementation is very faint and intermediate between Types I and II at the points where no carbon deposit has formed.
....	.....	....	.....	Very thin cemented zone.
....	.....	....	.....	. No cementation.
....	.....	....	.....	Very thin cemented zone.
....	.....	....	.....	No cementation.
....	.....	....	.....	No cementation.
0.5	0.5	According to Type II. .	1.1	......
0.3	0.4	According to Type II. .	1.1	......
0.1	0.15	According to Type II. .	1.1	......
0	1	According to Type I. . .	0.5	......
0	0.6	According to Type I. . .	0.3	......
0.25	0.4	According to Type II. .	1	......

Number	Carburizing gas used	Length of cementation (hours)	Pressure of carburizing gas (mm. mercury)	Temperature (degrees C.)	Volume of gas used (liters)	State of the surface of the steel cylinders after the cementation	Thickness of the	
							Total thickness (mm.)	Thick- Hyper-eutectic (mm.)
25	Methane........	5	462	900	7	Abundant deposit of pulverulent carbon....	0.6	0.1
26	Illuminating gas.	5	470	900	8	Slight deposit of carbon	0.8	.....
27	Illuminating gas.	5	463	900	8	Very slight deposit of carbon..............	0.5	.....
28	Ethylene........	5	760	1000	7	Abundant deposit of carbon...............	2.0	0.6
29	Ethylene........	5	462	1000	7	Abundant deposit of carbon...............	1.8	0.5
30	Carbon monoxide	5	760	1000	7	No deposit of carbon...	2.0	.....
31	Carbon monoxide	5	462	1000	7	No deposit of carbon...	1.4	.....
32	Methane........	5	760	1000	7	Not very abundant deposit of powdery carbon.................	2.0	0.7
33	Methane........	5	466	1000	7	Not very abundant deposit of powdery carbon.................	2.0	0.7
34	Illuminating gas.	5	760	1000	10	Slight deposit of carbon.	1.5	.....
35	Illuminating gas.	5	460	1000	10	Very slight deposit of carbon...............	1.2	.....
36	Ethylene........	3	760	1100	5	Very abundant deposit of pulverulent carbon.	2.9	1.6
37	Ethylene........	3	458	1100	5	Very abundant deposit of pulverulent carbon.	2.0	0.9
38	Carbon monoxide	3	760	1100	5	No deposit of carbon...	3.0	.....
39	Carbon monoxide	3	461	1100	5	No deposit of carbon...	3.0	.....
40	Methane........	3	760	1100	5	Deposit of compact carbon................	2.6	1.2
41	Methane........	3	463	1100	5	Deposit of compact carbon................	2.5	1.3
42	Illuminating gas.	3	760	1100	7	Very slight layer of pulverulent carbon.......	2.1	.....
43	Illuminating gas.	3	459	1100	7	Very slight layer of pulverulent carbon.......	2.1	.....
44	Carbon monoxide	3	760	1100	9	No deposit of carbon...	4.0	.....
45	Carbon monoxide	10	760	1100	9	No deposit of carbon...	4.0	.....
46	Ethylene........	3	760	1100	1	Slight deposit of carbon.	......	.....
47	Ethylene........	3	760	1100	15	Very abundant deposit of pulverulent carbon.	4.5	2.5
48	Ethylene........	10	760	1100	11	Very abundant deposit of pulverulent carbon		

cemented zone		Distribution of the carbon in the cemented zone	Maximum concentration of carbon (cem. zone), percent.	Remarks
ness of zone				
Eutectic (mm.)	Hypo-eutectic (mm.)			
0.2	0.3	According to Type II..	1	....
....	0.8	According to Type II..	0.8	The cemented zone has a structure already approaching Type I.
....	0.5	According to Type II..	0.6	The cemented zone has a structure already approaching Type I.
0.4	1.0	According to Type II..	1.3	The "concentration-depth" diagram and a micrograph are reproduced further on.
0.4	0.9	According to Type II..	1.3	....
....	2.0	According to Type I...	0.35	A micrograph of this zone is reproduced further on.
....	1.4	According to Type I...	0.24	....
0.3	1.0	According to Type II..	1.3	....
0.3	1.0	According to Type II..	1.3	....
0.2	1.3	Intermediate between Types I and II......	0.9	....
....	1.2	Intermediate between Types I and II......	0.85	Approaches Type I more nearly than the preceding, lacking the eutectic zone.
0.4	0.9	According to Type II..	1.3	....
0.4	0.7	According to Type II..	1.3	....
....	3.0	According to Type I...	0.18	....
....	3.0	According to Type I...	0.12	....
0.4	1.0	According to Type II..	1.3	The "concentration-depth" diagram for this zone is reproduced further on.
0.4	0.8	According to Type II..	1.3	....
0.3	1.8	Intermediate between Types I and II......	0.9	....
0.3	1.8	Intermediate between Types I and II......	0.9	....
....	4.0	According to Type I...	0.3	....
....	4.0	According to Type I...	0.27	The "concentration-depth" diagram for this zone is reproduced further on.
....	.....	According to Type II..	0.9	....
0.4	1.5	According to Type II..	1.5	....
....	.....	Hyper-eutectic steel to the axis of the cylinder.	1.5	Hyper-eutectic cementation to the axis of the cylinder.

thermo-electric couple, the joint of which was introduced into the porcelain tube *B*, closed at the extremity projecting into the interior of the tube *A*.

The apparatus *H*, *R*, *N* . . . served to lower the pressure of the gas in the cementation chamber *A* to a definite and constant value. Its manner of operation is quite obvious.

The cemented specimens of steel were allowed to cool slowly in the furnace, then cut normally to the axis, polished, etched with a 4% solution of nitric acid in amyl alcohol, and observed under the microscope. In the cases in which the cemented zone was deep enough, we also made gravimetric carbon determinations on the material obtained on the lathe from successive layers of the cylinders, half a millimeter thick, in the manner already described.

The results of the forty-eight experiments are collected in the foregoing tables.

In order to explain clearly the designations "Type I" and "Type II" in the twelfth column of the tables, relative to the distribution of the carbon in the cemented zones, I must refer to the micrographs and "concentration-depth" diagrams of some of the more characteristic zones.

In the following table are collected the results of the gravimetric determinations of carbon made on successive layers, 0.5 and 0.75 mm. thick, obtained in the manner already indicated from the cylinders of steel cemented in Experiments 28, 40 and 45:

Experiment 28 Cementation with 7 liters of ethylene at 1000° for 5 hours		Experiment 40 Cementation with 5 liters of methane at 1100° for 3 hours		Experiment 45 Cementation with 9 liters of carbon monoxide at 1100° for 10 hours	
Depth, mm.	Carbon, percent.	Depth, mm.	Carbon, percent.	Depth, mm.	Carbon, percent.
0.25	1.30	0.25	1.28	0.75	0.27
0.75	0.86	0.75	1.30	1.50	0.21
1.25	0.52	1.25	1.02	2.25	0.16
1.75	0.26	1.75	0.82	3.00	0.11
2.25	0.08	2.25	0.58	....	....
....	....	2.75	0.21	....	....

The same data are represented graphically in the accompanying "concentration-depth" diagrams of Figs. 23, 24 and 25.

From the numerical data, and still more from the curves of the three diagrams, the characteristics which distinguish clearly the cemented zone obtained with carbon monoxide in Experiment 45 from the other two, obtained by cementing the same steel under analogous conditions with ethylene and methane respectively, are evident. These differences come out still more clearly in the comparison of the two photograms of Figs. 26 and 27, the first of which reproduces, with an enlargement of 75 diameters, the microstructure of the cemented zone obtained with ethylene at 1000° C. in Experiment 28.

The second photogram (Fig. 27) refers to the cemented zone obtained with carbon monoxide at 1000° C. in Experiment 30, a zone for which the "concentration-depth" curve has a form perfectly similar to that of Fig. 25 (cementation with carbon monoxide at 1100° C.).

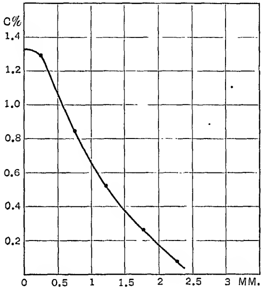

FIG. 23.

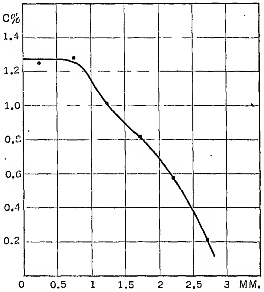

FIG. 24.

From the examination of the diagrams and of the micrographs we see that we can distinguish two types of cemented zones, characterized by a different distribution of the carbon in their successive layers:

1. The cemented zones belonging to the first *type*, corresponding to the diagram of Fig. 25 and to the micrograph of Fig. 27, are characterized by the fact that in them the concentration of the carbon does not reach at any point (and not even at the periphery) its value in the eutectic (0.9%), and diminishes *progressively* and in a *uniform and slow* manner as we pass from the surface toward the interior of the cemented pieces.

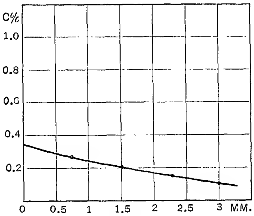

FIG. 25.

In the experiments summarized in the two tables of pages 78–81, the zones of this first type correspond always and only to cementation carried out with pure carbon monoxide, in which the formation of any deposit of free carbon on the surface of the steel cylinders does not manifest itself.

2. The cemented zones belonging to the *second type*, corresponding to the diagrams of Figs. 23 and 24 and to the micrograph of Fig. 26, are characterized by a highly carburized external layer in which the concentration of the carbon surpasses its value in the eutectic (0.9%).

Below this first external layer the concentration of the carbon diminishes in a *non-uniform* manner; we shall see later, on the basis of more precise experiments, what the distribution of the carbon characteristic of zones of this type is. At present it is enough to point out the fact, resulting clearly from the micrograph of Fig. 26, as also from that reproduced some pages back from the work of Bruch (which also refers to cementation carried out with acetylene), that in zones of this type there are always observed three distinct strata, more or less clearly separated from each other; an external hyper-eutectic layer, followed by an intermediate eutectic layer (with 0.9% of carbon), the thickness of which does not exceed half a millimeter, followed in its turn by an internal hypo-eutectic layer.

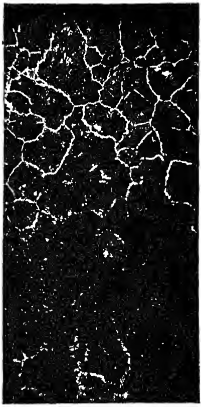

FIG. 26.

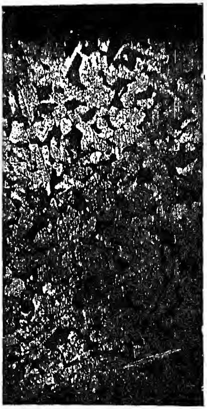

FIG. 27.

In the experiments (1 to 48) summarized in the two large tables, the zones of the second type (more or less deep, according to the temperature used) are always found in cementations carried out with ethylene and with methane, and are always accompanied by a deposit of free carbon on the surface of the steel specimens. Thus, in Experiments 11, 12 and 13 (carried out by cementing with ethylene at 780°), in which the deposit of free carbon was formed only in some regions of the steel cylinders, the cemented zones assume clearly the characteristics of the second type only in the parts on which the carbon has deposited, while in the other parts they assume an aspect intermediate between the first and the second type.

In Experiments 34, 35, 42, and 43, carried out by cementing with the illuminating gas whose composition was given, there are obtained (as is indicated in the twelfth column of the table) cemented zones in which the distribution of the carbon is intermediate between the first and the second types. This intermediate type of cemented zone, the practical importance of which we shall see later, is characterized by the lack of the external hyper-eutectic zone, which always characterizes the second type, but it differs from the first type in the fact that the carbon reaches in it a higher concentration, which remains equal (or quite close) to 0.9% in a more or less thick external layer formed of pearlite alone, and then gradually diminishes in the layers lying beneath. We shall see later how this intermediate type of cemented zone can be always obtained by carrying out the cementation with carbon monoxide in the presence of solid cements or in the presence of definite quantities of hydrocarbons.

It is evidently this second case which manifests itself in cementations carried out with the illuminating gas whose composition was given.

Returning to the cementation carried out with pure carbon monoxide, we can at once draw some conclusions:

The concentration of carbon in the cemented zone depends on various elements, and especially on the temperature, on the pressure of the gas, and on the velocity of the current of gas.

This follows very clearly from the experiments which I have summarized in the tables, as is seen from the following considerations:

1. All other conditions being equal, the concentration of the carbon in the cemented zone is *smaller* the *higher* the temperature. To become convinced of this, compare with each other the results of Experiments 22, 30, 38 and 45.

2. All other conditions being equal, the concentration of the carbon in the cemented zone is *smaller* the *lower* the pressure of the gas. To become convinced of this, compare the results of Experiment 22 with those of 23, those of 30 with those of 31 and those of 38 with those of 39.

3. All other conditions being equal, the concentration of the carbon in the cemented zone increases when the quantity of pure carbon monoxide which comes in contact with unit of surface of the steel during the cementation increases. A comparison of the results of the three experiments, 38, 44 and 45, proves this, it being noted that in all three the total surface of the steel subjected to cementation was the same (60 sq. cm.).

These phenomena are easily explained when we take into account first of all the fact that in all the cementations carried out with carbon monoxide at a temperature higher than 850° C., and passing the gas over the pieces of steel with the velocity used by us, no deposit whatever of free carbon is formed, and the surface of the pieces of cemented steel remains perfectly clear and shiny. This shows that the free carbon which is formed in the transformation of the carbon monoxide into carbon dioxide dissolves entirely in the γ-iron with which it comes in contact. In other words, under the conditions above indicated the velocity with which the free carbon is formed is lower than that with which this carbon passes into solution in the γ-iron as austenite or martensite (according to the temperature).

Granted this, it is evident that, under these conditions, a new variable will enter into the equilibrium of the reaction

$$2CO \rightleftarrows CO_2 + C$$

to which the carburizing action of carbon monoxide is due. This new element is the concentration of the carbon (appearing in the second member) in its solution in the γ-iron, for *all* of the carbon which is liberated passes into the state of solution.

The carbon which is liberated by the catalytic action of the iron on the carbon monoxide, according to the reaction written above, therefore dissolves completely in the external layers of iron (which, at the temperature worked with, is in the state of γ-iron) until it reaches the concentration which corresponds to the state of equilibrium of the system $CO : CO_2 : C$ in solution in γ-iron at the temperature and pressure experimented with.

The fresh carbon monoxide which comes into contact with the steel should then undergo the same decomposition, but to a lesser degree, for, by yielding fresh carbon to the external layers of steel, the concentration of this element is increased so that under the new conditions the equilibrium will exist for a smaller quantity of carbon dioxide and hence for a less extensive decomposition of the carbon monoxide. In this case, the concentration of the carbon in the external layers of the steel should increase rapidly and the carbon itself should diffuse into the layers lying beneath by simple difference in concentration, necessarily following the same laws which govern the diffusion of the carbon in the cementation with solid carbon. But we have seen that the distribution of the carbon in the carburized zones obtained by cementing steel with solid carbon[1] differs profoundly from that which is found in the zones obtained by cementing with carbon monoxide. In the first the concentration of the carbon decreases rapidly as we pass from the external layers to those which are deeper and deeper, following exactly the course which corresponds to the diffusion of a dissolved substance by "difference of concentration," but in the steels obtained by cementing with carbon monoxide the concentration of the carbon varies so little from the external layers of the carburized zone to the deeper ones (see Experiment 45 and the diagram of Fig. 25) that it is not possible to admit that the carbon

[1] See, for example, the experiments on a large scale previously cited, p. 74.

has diffused into the mass of γ-iron by a simple phenomenon of solution due to the difference in concentration of the various layers, and we cannot but recognize that another cause has co-operated in producing the diffusion. This cause is evidently the penetration of the carbon monoxide into the steel.

When the gaseous mixture of CO and CO_2 which is in equilibrium at a given temperature with the carbon dissolved in the exterior carburized layer of the steel comes in contact with the steel of the internal layers, in which the concentration of the carbon is smaller and with which it is, therefore, no longer in equilibrium, it yields to their γ-iron a little carbon, increasing its content in carbon dioxide; this causes it to oxidize anew a part of the more highly concentrated carbon contained in the exterior layers—and so on. It therefore results that carbon monoxide, mixed with varying quantities of carbon dioxide, diffusing into the mass of γ-iron, merely equalizes in it the concentration of the carbon, and this within certain limits depending on the relative velocities of the various reactions and on the various phenomena of solution of the carbon and of diffusion of the gases. It is therefore to be foreseen that all causes which tend to shift toward the right the reaction

$$2CO \rightleftarrows CO_2 + C$$

must necessarily increase in the γ-iron of the cemented zone the concentration of carbon, to correspond to the new conditions of equilibrium.

Among such causes, as is well known, must be numbered especially the lowering of the temperature and the raising of the pressure, and this because of the fact that the reaction is (in the direction indicated) *exothermic* and takes place with a decrease in volume. As we saw a short time back, these predictions are fully confirmed by experiment.

It is therefore easy to explain, on the basis of what we have just said, the experimental fact that the concentration of the carbon in the cemented zone increases, all the other conditions remaining the same, when the quantity of carbon monoxide coming in contact with a given surface of steel in the unit of time is increased. In fact, while both the velocity of penetration of the carbon by solution into the γ-iron and that of the diffusion of the carbon monoxide into the metallic mass remain constant in this case, on account of the constancy of the temperature and of the pressure, the concentration of the carbon monoxide (which is more rapidly renewed) is higher and hence the quantity of carbon which is deposited in the cemented zone of a given thickness is greater.[1]

[1] I would remark that the gaseous mixtures of carbon monoxide and carbon dioxide which are, above 1000° C., in equilibrium with free carbon (wood charcoal) are richer in carbon monoxide than those which are in equilibrium with solid solutions of cementite in iron containing less than 0.9% of carbon. This results not only from the indirect proofs which I adduce in what follows, but from many direct determinations which I have thus far but briefly made public (see *Rendiconti della Società Chimica di Roma*, 1908, Vol. VI, No. 16).

Besides establishing these important facts, the experiments summarized in the tables on pages 78–81 enable us to make some other quite interesting observations. They not only confirm the well-known influence of temperature on the velocity of cementation, but enable us to show that this influence manifests itself just as well in cementations carried out with ethylene or methane as in those carried out with carbon monoxide; but, while in the latter the increase in depth of the cementation due to rise in temperature is accompanied by a decrease in the concentration of the carbon in the cemented zone, in the cementations with ethylene or methane the cemented zone obtained in a given time, although also increasing markedly in thickness with rise in temperature, other conditions remaining constant, maintains about the same concentration and the same distribution of the carbon in the three characteristic layers of which I have already spoken.

As to the influence of pressure on the velocity of cementation I shall have occasion to give later more complete data.

If we compare the results of Experiments 36 and 47, carried out by cementing with ethylene at constant temperature (1100°) under constant pressure (760 mm.) during the same length of time (three hours), but varying the *quantity* of carburizing gas used (from five to fifteen liters), we see that the *depth* of the cementation, all other conditions being equal, increases greatly with increase in the *volume* of gas used. In all cases an abundant deposit of free pulverulent carbon is formed; it is therefore evident that the penetration of the carbon can not be due solely to the carbon deposited diffusing into the iron, by difference in concentration, since in this case the diffusion should take place in an identical manner in the two experiments. It is therefore evident that in the cementation carried out with gaseous hydrocarbons, diffusion of the gas "as such" into the iron also comes into play.

Finally, the experiments with which I am now dealing show also how a true process of cementation of steels of low carbon content cannot take place at temperatures below 780°, a result which is in apparent contradiction with those of many earlier experiments.[1]

The explanation of this apparent contradiction is better developed in a communication which I presented shortly afterward,[2] in collaboration with Doctor Carnevali, before the Chemical Society of Rome. The cause of the apparent disagreement is to be found in the different methods of observation used to establish and measure the cementation, and to the consequent varying significance attributed to the word "cementation." In fact,

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[1] See especially Charpy, *Comptes Rendus de l'Académie des Sciences*, Vol. CXXXVII, pp. 120–122; Giolitti, *Gazz. Chimica Italiana*, September, 1908.

[2] F. Giolitti and F. Carnevali, *Sul limite inferiore dell'intervallo di temperatura entro il quale si compie il processo della cementazione* (*Rend. della Società Chimica di Roma*, 1908, Vol. VI, No. 17).

Charpy and all the other experimenters who have affirmed the possibility of the cementation of iron at temperatures below 700° have based this assertion on the results of simple *gravimetric determinations* (direct or indirect) of the carbon which has penetrated by diffusion into the iron, without taking care to learn in what state this carbon is present in the iron and what effects it produces on the nature and on the structure of the metal into which it has penetrated; in other words, they have meant by "cementation" any process whatever of "carburization" of iron.

We, on the other hand, making use essentially of microscopic examination to determine and measure the cementation (although often accompanying it with chemical analyses) spoke of the existence of a cemented zone only in the cases in which we could establish the formation of a layer, more or less thick, of *a true steel proper*, *more highly carburized* than the steel subjected to the cementation; therefore we have meant to indicate by the words "cemented zone" a zone not only of higher carbon content but also possessed of the structure characteristic of a true proper steel having a higher carbon content.

Now, since it is known that this structure results from the segregation in the iron, during cooling, of the solid *solution* of the carbon to the state of cementite, and since this solution can not be formed at a temperature lower than 780° (α-iron), it is evident that it is impossible to observe any true *cementation* proper (in the sense meant by us) at a temperature below 780° C.

It is easy to explain the superficial carburization observed at relatively low temperatures (500°–600°–700°), by other experimenters, by two well-known phenomena:

1. All the experimenters who have affirmed the possibility of cementing iron at temperatures below 700° used as cementing agent either carbon monoxide or substances capable of evolving this gas, such as mixtures of carbon and barium carbonete. Now, by a mechanism analogous to that which I have already explained (see p. 87), the carbon monoxide diffusing into the iron deposits carbon there, even in the case when this carbon can not dissolve in the iron, such as when the iron is in the state of α-iron.[1] This carbon, however, whether it remains in the free state or forms a carbide of iron, does not impart to the metal the properties of a *more highly carburized true steel*, for the essential constituents of the latter (pearlite

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[1] It is well to point out that the quantity of carbon which a given weight of carbon monoxide can liberate is greater (within limits) the lower the temperature, being dependent upon the equilibrium of the reversible reaction.

$$2\,CO \rightleftarrows CO_2 + C$$

The carbon concentration is proportional to the concentration of the carbon dioxide at the equilibrium of the system $CO : CO_2 : C$. And this concentration, according to the results of the investigations of Boudouard (*Ann. de Chim. et de Phys.* [7], XXIV, pp. 5–85), while it is only 0.7% at 1100° C., is equal to 42% at 700°, 77% at 600° and 89% at 550°.

together with the remainder of the pre-existing ferrite, or pearlite and cementite) can come only from the segregation of iron-carbon solid solutions. There is in this case, therefore, no true cementation.

2. The carbon pre-existing in the cementing material or resulting from the decomposition of carburizing compounds (such as carbon monoxide, hydrocarbons, etc.), coming in contact with the surface of the steel can form there a fine layer of free cementite; this, however, does not diffuse into the soft steel lying below, which preserves its primitive structure. This fact we were able to establish conclusively, as is shown by the micrographs reproduced in the paper which I have already cited.[1] In this case also, therefore, the process of carburization which manifests itself at a relatively low temperature is not a true cementation.

Having recognized the "discontinuity" of the distribution of the carbon in the cemented zones of high carbon content which are obtained with the cements commonly used, and which all give strong carburizations, I very quickly came to recognize an interesting relation between this discontinuity and a phenomenon well known and important for the practice of the cementation of machine parts; I refer to the phenomenon of "exfoliation" of pieces of soft steel superficially cemented and hardened.

Having had occasion to examine the "distribution" of the carbon in a very large number of pieces cemented and quenched under various conditions under my direction (especially drills, bits, toothed wheels, rings and cups for ball bearings, axles, etc.), many of which subsequently exfoliated in service, I was able to establish the causes of the discontinuities observed and, therefore, of the phenomena referred to, and this allowed me to establish some useful rules to avoid both the one and the other.

The first of these observations were communicated briefly to the Chemical Society of Rome in 1908.[2] These phenomena, studied with greater experimental accuracy, in collaboration with Doctor Tavanti, form the subject of a more extensive paper published in the following year.[3]

The phenomenon of the "exfoliation" or "splitting" of cemented steels is well known to all who have had occasion to examine machine pieces of "case-hardened" soft steel fractured in service. While in hard, homogeneous, quenched steels the surfaces of fracture always have a characteristic conchoidal form, soft steels carburized by cementation only in a surface layer more or less deep and subjected to a homogeneous hardening present surfaces of fracture with totally different characteristics. In fact, in this second case the steel breaks along a surface almost parallel to the external surface of the cemented piece, so that, instead of metallic lenticular masses detaching themselves from it as in the case of homogeneous steel, whole surface "leaves," more or less thick according to the depth to which the cementation has extended, detach themselves. Of this phenomenon, which experts know well and characterize by saying that a cemented piece "exfoliates," a very clear example is furnished by an automobile part of cemented soft steel reproduced in Fig. 28, taken from a work of Portevin.

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[1] *Rend. Soc. Chim. di Roma*, 1908, No. 17.

[2] F. Giolitti, *Sul fenomeno della sfaldatura negli acciai cementati, e sui mezzi per evitarlo* (*Rend. della Soc. Chim. di Roma*, 1908, No. 17).

[3] F. Giolitti and G. Tavanti, *Ricerche sulla fabbricazione dell'acciaio cementato*, III: Sui fenomeni di liquazione che si verificano negli acciai cementati (*Gazz. Chim. Ital.*, 1909, Vol. XXXIX, Part II).

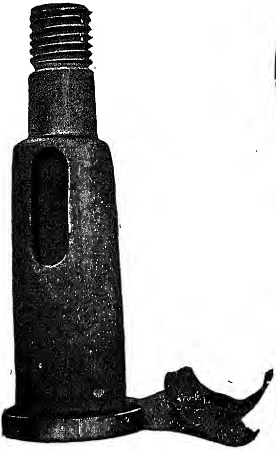

Fig. 28

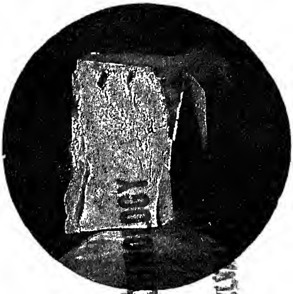

Fig. 29.

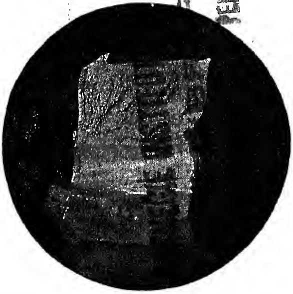

Fig. 30.

Another very clear example of the phenomenon with which I am dealing is that reproduced in Fig. 29, which represents a fragment of a large drill of cemented soft steel. There appears very clearly, at *a*, on the fractured tooth of the section, the superficial "fold" of fine structure, sharply separated from the mass of coarser structure lying beneath.

Every expert knows that the surface along which a piece of steel "exfoliates" corresponds to a sharp surface of separation between two zones of the steel possessing a different structure or "grain." Thus in Fig. 30, which represents another surface of fracture of the same drill, the variation of the "grain" is visible at the upper edge of the surface of fracture, by chance so obtained as to avoid exfoliation.

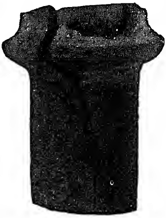

Fig. 31.

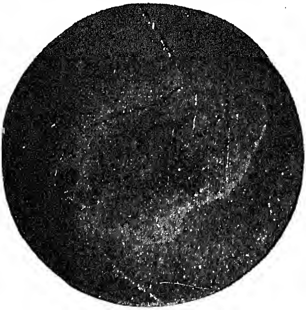

Fig. 33.

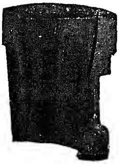

Fig. 32.

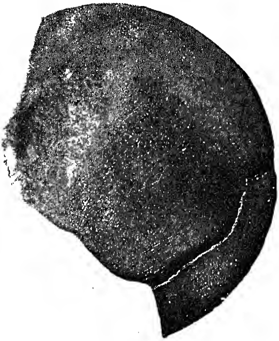

Fig. 34.

Since it is known that steels of different composition, hardened under identical conditions, show surfaces of fracture characterized by different structure or "grain" it was quite natural to suppose that the exfoliation of steels cemented and subjected to a homogeneous hardening would correspond with sudden variations in the composition of the steel. A more accurate study of the phenomenon has fully confirmed this hypothesis, showing that sudden variations in the composition of the steel are certainly the cause of the exfoliation of the cemented steels, and that the variations in composition producing these effects are sudden variations in the concentration of the carbon.

The conclusions thus briefly summarized are the result of a large number of observations, lasting through several years, on cemented pieces which had "exfoliated" in service.

In making observations, the metallographic examination of the pieces studied has been of valuable, if not indispensable, assistance. For example in Figs. 31 and 32 are reproduced (about natural size) two fragments of cemented and quenched soft steel, the axle of the rear wheel of a bicycle. The appearance of the fracture of this piece, broken in service, is exactly characteristic of the "exfoliation" of steels cemented and hardened homogeneously.

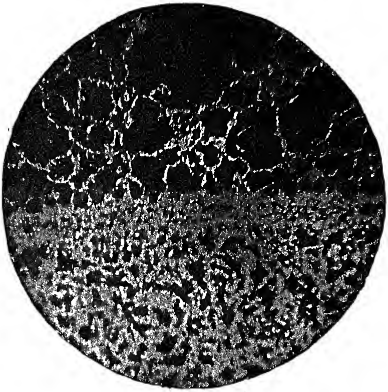

FIG. 35.

Fig. 33 reproduces, with an enlargement of 3.7 diameters, the plane section, normal to the axis of the cylinder, constituting the lower base of the fragment reproduced in Fig. 31. This section was made after having heated the cylinder of steel for about one hour at 900° out of contact with the air; it was polished with chromium oxide and etched with a 5% alcoholic solution of picric acid. In the photograph it is seen clearly that the surface of fracture corresponds to a surface along which the structure of the steel varies suddenly. The same fact comes out even more clearly in Fig. 34, which reproduces (with an enlargement of 3.7 diameters) the section, made and prepared in a manner analogous to the preceding, which forms the upper base of the piece reproduced in Fig. 32.

In both sections, the variation in the structure is especially evident at the points to which the fracture has not yet extended, and at these points it is easy to recognize that the line of separation between the zones of different structure is but the continuation of the line of fracture.

The two figures, 35 and 36, represent with a greater enlargement (60 diameters) two short stretches of the line of demarcation between the two zones of different structure of the section reproduced in Fig. 33. The first reproduces a part of this line to which the fracture has not yet extended, while the second reproduces a part in which the fracture has already begun. In both micrographs, the proportion between the areas occupied by the pearlite and by the ferrite, respectively, shows that the sudden variation in the structure of the steel which manifests itself along the surface of fracture corresponds to a sudden variation in the concentration of the carbon. In the special case to which I am now referring, the concentration changes rapidly across the surface of fracture, from 0.6–0.7% (toward the periphery) to less than 0.2% (toward the nucleus of the cemented piece).[1]

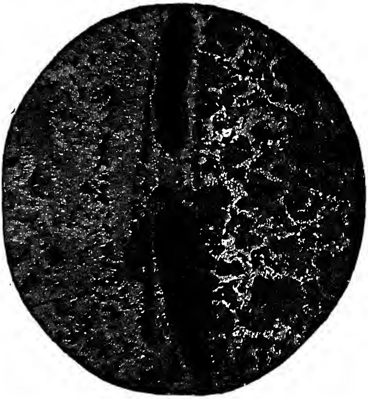

FIG. 36.

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[1] For greater details on the characteristic structures of the micrographs just reproduced, see F. Giolitti and G. Tavanti, *Ricerche sulla fabbricazione dell'acciaio cementato*, VII (*Atti della R. Accademia delle Scienze di Torino*, 1910).

Since, as already stated, I have observed similar coincidences in a large number of cases between the surfaces of exfoliation and the surfaces corresponding to sudden variations in the concentration of the carbon in the cemented zones, the importance of a more precise study of these variations in concentration by gravimetric analyses of the successive layers of these zones was evident.

The analyses of layers 0.5 to 1 mm. thick could not furnish sufficiently precise data, for they could indicate only the *mean* composition of layers in each of which the concentration of the carbon often varied *discontinuously* from the exterior toward the interior; this follows clearly from the data collected in the tables of pages 78–81. Thus, for example, the eutectic zone has a thickness ranging from 0.1 to 0.3 mm., so that it is certain that by taking for the analyses layers 0.5 mm. thick, material of adjacent zones was included in the analysis. *Not one* of the layers analyzed gave the value of constant carbon concentration (0.9%) characteristic of this zone. To be able to establish on the "concentration-depth" diagrams the important discontinuity, characterized by a horizontal portion corresponding to the composition of the eutectic zone joined more or less abruptly with the steeply inclined arms of the curve corresponding to the adjacent hypo-eutectic and hyper-eutectic zones, it is evidently necessary that *two or more* of the layers analyzed should fall entirely within the eutectic zone.

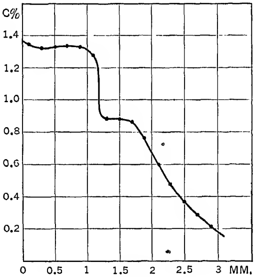

Fig. 37.

It is clear, therefore, that the curves which I have reproduced above can not show with sufficient distinctness the discontinuities characteristic of the cemented zones. For this it is necessary to analyze successive layers of these zones not thicker than 0.1–0.2 mm.

A first series of carbon gravimetric determinations, made on the material obtained from successive layers (0.2 mm. thick) of a cemented zone obtained by carburizing a cylinder of soft steel (0.08% of carbon) for four hours at 1050° C., and then allowing it to cool very slowly, showed at once the phenomena of discontinuity. The results of these analyses, which I communicated in a preliminary paper presented before the Chemical Society of Rome in 1908, are collected in the manner which I have already explained in the "concentration-depth" diagram reproduced in Fig. 37.

It is easy to see how this diagram confirms fully the results of the microscopical examination. To become convinced of this, examine the micrographs Fig. 26 (cementation five hours at 1000° C. with ethylene, followed by slow

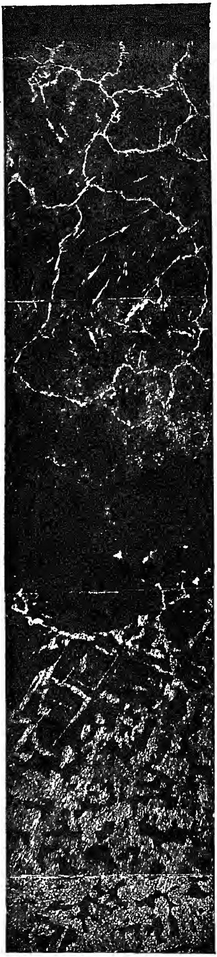

FIG. 38.

cooling), Fig. 18 (cementation seven hours with acetylene at 1050° C., likewise followed by slow cooling) and Fig. 38. This last figure shows a cemented zone obtained under the same conditions as that of Fig. 37 (ethylene at 1050° C.) but during five hours instead of four. From the micrographs as well as from the diagram it is evident that the carburized zones obtained by cementing soft steel with volatile hydrocarbons at a high temperature (1000–1100° C.) and then allowing the cemented pieces to cool slowly, are subdivided into three strata characterized by their carbon content and by their microstructure.

The first layer, clearly hyper-eutectic, is characterized by the presence of cementite and pearlite; in it the carbon content varies from 1.27% to 1.33%, markedly higher than the value for pearlite (0.9%).

The second layer, generally less than 0.5–0.6 mm. thick, is formed of pearlite alone; in it, therefore, the concentration of the carbon is uniform and equal to about 0.9%. This layer appears clearly in Fig. 37, corresponding to the intermediate horizontal portion of the "concentration-depth" curve.

This second layer is followed by a third, a hypo-eutectic layer, characterized, therefore, by the presence of pearlite and ferrite, in which the carbon content (always less than 0.9%) diminishes at first rapidly, then more slowly, toward the interior of the cemented piece. The sudden variations in the concentration of the carbon in the layers of the passage between the hyper-eutectic zone and the eutectic zone and between the latter and the hypo-eutectic zone are evident either from the micrographs (Figs. 18, 26 and 38) or from the diagram, Fig. 37. Thus, referring to the diagram, in which the values of the concentration of the carbon are shown with greater precision, we see that the carbon content at first remains almost constant for a thickness of more than a millimeter, oscillating only between 1.27 and 1.33%, then falls from 1.27 to 0.88% in the space of a quarter of a millimeter, then

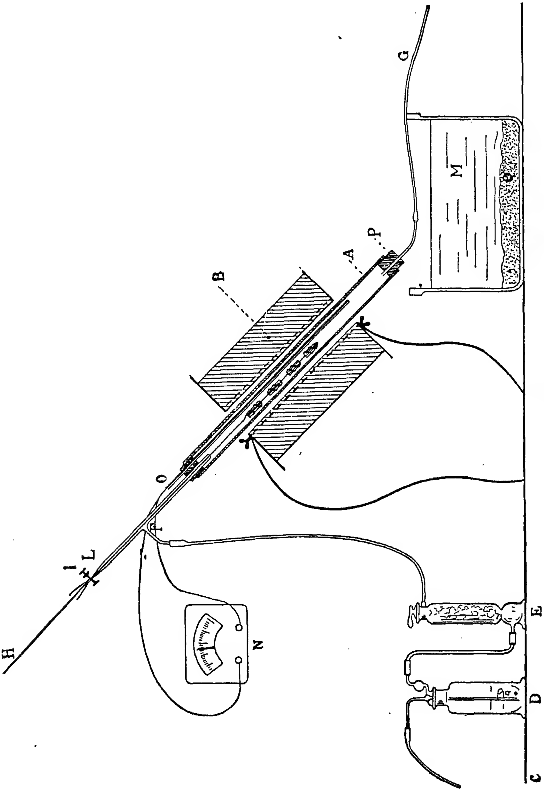

FIG. 39.

again remaining almost absolutely constant between 0.88% and 0.86% in the eutectic zone, more than half a millimeter thick, and diminishes rapidly from 0.86% to 0.61% in the successive four tenths of a millimeter.

There are thus established accurately the phenomena of discontinuity in the "distribution" of the carbon in the cemented zones, to which, as I have already said, experiment shows that the "exfoliation" of cemented steels is due.

A series of earlier investigations[1] had already led me to explain some analogous phenomena manifesting themselves in cast iron (malleableized castings) by the theory of processes of "liquation" of the cementite and the ferrite, which are effected during the slow cooling which follows the chemical treatment. It was therefore quite natural that I should attempt to determine whether the phenomena observed in cemented steel are not due to the same cause.

Positive results were obtained by studying, in collaboration with Doctor Tavanti, the influence of the velocity of the cooling following the cementation and preceding quenching, on the distribution of the carbon in the cemented zones.[2] Fig. 39 represents the apparatus used for these investigations to quench the specimens of steel at the same temperature as that of the cementation, avoiding any slow cooling before the quenching.

Steel of the following composition:

Carbon	0.26 percent.
Manganese	0.54 percent.
Sulphur	0.02 percent.
Phosphorus	0.02 percent.

was cut in the form of cylinders 10 mm. in diameter and 100 mm. long. These were fastened to a nickel wire which was clamped by the screw pinchcock *I* in the rubber tube *L*, and thus were held in place in the glazed porcelain tube *A*, inclined at an angle of 45° and heated in the Heraeus furnace *B* at a constant temperature, measured by means of an electric pyrometer *OFN*.

The carburizing gases, purified and dried in *C*, *D*, *E*, pass through the tube *A*, come in contact with the specimens to be cemented, and issue from the tube *G*. When it is desired to quench the specimens, it is merely necessary to remove the stopper *P* and loosen the clamp *I*; the nickel wire is freed and the specimens fall into the vessel *M* containing water at 12°. On the bottom of the vessel is placed a layer of sand to prevent the cylinders of steel from breaking it.

The tempered steel cylinders were brought back for five minutes to 700°, out of contact with the air;[1] then, after they had been straightened, and adjusted in the lathe, co-axial layers 0.1 mm. thick were removed, and the carbon in them determined by combustion.

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[1] See F. Giolitti, *Sulla fabbricazione della ghisa malleabile*, I (*Rend. della Società Chimica di Roma*, 1908); and F. Giolitti, F. Carnevali and G. Gherardi, *Id.*, Note II (*Atti della R. Accademia dei Lincei*).

[2] F. Giolitti and G. Tavanti, *Ricerche sulla fabbricazione dell' acciaio cementato*, III (*Gazzetta Chim. Italiana*, 1909).

Seven such experiments of cementation and quenching were carried out under different conditions, especially as regards the relations between the temperature of cementation and that of the corresponding quenching and, therefore, the extent and length of the slow cooling following the cementation and preceding the quenching, as is indicated in the following table:

Number	Gas used as cement	Length of cementation (hours)	Temperature of cementation	Length slow cooling following cement. and preceding quenching (min.)	Extent of interval of cooling	Temperature of quenching in water at 12° (degr. C.)	Volume of carburizing gas used (liters)
1	Ethylene	4	1000° C.	32	250° C.	750°	6.6
2	Ethylene	4	1000°	0	0	1000°	6.25
3	Ethylene(*a*)	1	1000°	15	200°	800°	3.0
4	Ethylene	4	800°	0	0	800°	6.25
5	Mixture of CO with 3.1% of ethylene.	4	1000°	22	250°	750°	6.25
6	Mixture of CO with 3.1% of ethylene.	4	1000°	0	0	1000°	6.0
7	Mixture of CO with 3.1% of ethylene.	4	800°	0	0	800°	6.25

(*a*) The steel used in this 3rd experiment contained only 0.04% of carbon.

The results of these experiments are represented graphically, in the manner already explained, in the seven "concentration-depth" diagrams reproduced herewith (Figs. 40–46).

Since a very large number of earlier experiments (some of which I have in part summarized[2]) have shown that the variation in the concentration of the carbon in the cemented zones obtained by the action of gaseous hydrocarbons such as ethylene is analogous to that which is observed in the cemented zones obtained by means of the solid cements usually employed in practice, containing organic substances and cyanides, we can apply to the study of the phenomena of exfoliation which manifest themselves in practice the deductions drawn from the results of the first four of the experiments just given.

The examination of the first diagram (Fig. 40), representing the variations in the concentration of the carbon as functions of the depth in the specimen cemented with ethylene at 1000° and quenched at 750° after having slowly cooled to this temperature, shows directly a characteristic phenomenon which differentiates clearly the cemented zone obtained by this treatment from that which is obtained when, all the other conditions remaining equal, the cemented specimen is quenched at the same temperature as that at which the cementation was effected.

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[1] In the original memoir (through a typographical error) the temperature of heating is given as 900° instead of 700° C.

[2] See Giolitti and Carnevali, *Ricerche sulla fabbricazione dell'acciaio cementato*, II (*Gazz. Chim. Italiana*, 1908, Part II).

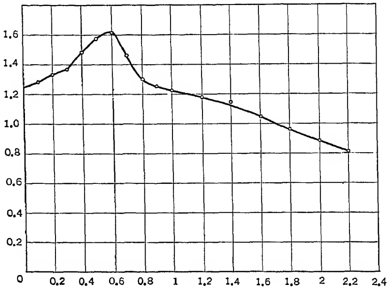

FIG. 40.

Comparing the diagram of Fig. 40 with that of Fig. 41, we see that while in the latter the concentration of the carbon *decreases* continuously and uniformly as we proceed from the surface toward the axis of the cemented

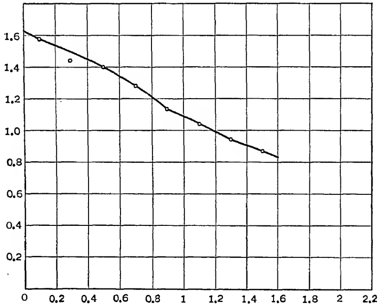

FIG. 41.

cylinder, in the first (proceeding in the same direction) the concentration, on the contrary, increases at first until it reaches a maximum at a depth of 0.6 mm., and then diminishes rapidly up to a depth of 0.8 mm., then decreasing considerably more slowly, so that in the whole succeeding interval of 1.4 mm. the concentration varies only between 1.2% and 0.81%.

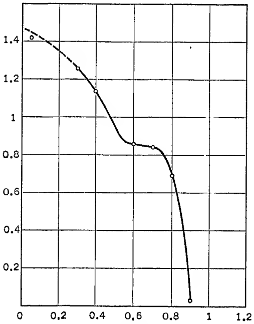

Fig. 42.

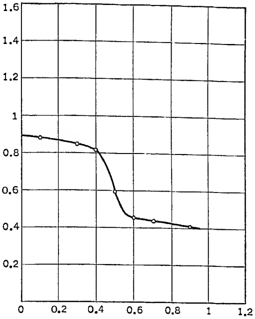

Fig. 43.

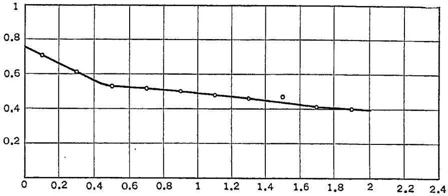

Fig. 44.

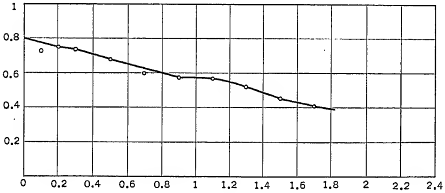

Fig. 45.

We evidently can not admit that this discontinuity in the concentration of the carbon can be due to the essentially *continuous* phenomenon of the diffusion of this carbon. Moreover, this discontinuity was not produced in the second experiment (Fig. 41), in which the cementation was carried out under identical conditions and in which the quenching at 1000° immediately after the cementation, has, so to speak, fixed the variations in the concentration of the carbon in the various layers exactly as produced by the process of diffusion of the carbon into the γ-iron. These variations are clearly continuous and uniform, as follows from the diagram, Fig. 41. We must admit, therefore, that the discontinuities which appear in the first case are due to a phenomenon different from the diffusion of the carbon and that it must take place in a phase of the process missing in the second experiment; this phase can evidently be only the slow cooling from 1000° to 750° which, in the first experiment, precedes the quenching.

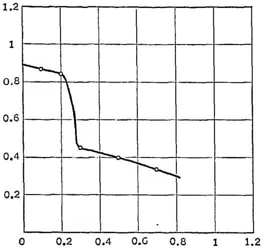

FIG. 46.

So much being known, it is not difficult to determine what are the phenomena which take place during the slow cooling of the cemented pieces, giving rise to the special distribution of the carbon, as shown in the diagram, Fig. 40.

For greater clearness, I refer to the well-known equilibrium diagram of the iron-carbon system, on which the values of the concentration of carbon are plotted on the axis of abscissas. And since, as follows from the diagram of Fig. 41, the concentration of the carbon in pieces cemented with ethylene at 1000° varies about inversely with the depth, passing from a maximum in the surface layer to a minimum (the carbon content of the homogeneous steel used) in the extreme internal limit of the cemented zone, we can make use of the abscissas to represent, besides the concentrations of the carbon in the various layers of the steel, the distances of the layers to which these concentrations correspond from the external surface of the cemented piece, noting that the numbers of the second series will run in the inverse direction to those of the first. Thus, in Experiment 2, the points of the line *AB* (Fig. 47)[1] corresponding to 1.63% of carbon will correspond also to the external surface of the cemented cylinder, while those of the vertical *PQ*, corresponding to 0.26% of carbon (content of the original homogeneous steel) will correspond also to the deepest layer to which the cementation has extended.

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[1] In the figure the relations of the segments representing the concentrations have been altered, so as not to render the figure too disproportionate. Thus, for example, the straight line *AB* should be more toward the right. The figure would correspond, therefore, to a shorter cementation.

The points of the verticals intermediate between these two will represent (at the various temperatures) the successive layers of the cemented zone and the corresponding concentrations of the carbon. All this holds as long as the continuity in the variations of the concentration of the carbon between the successive layers subsists; that is, as long as the temperature is, in the whole cemented zone, higher than the values represented by the points of the curves *CE* and *EN*, corresponding to the crystallization of ferrite and of cementite, respectively.

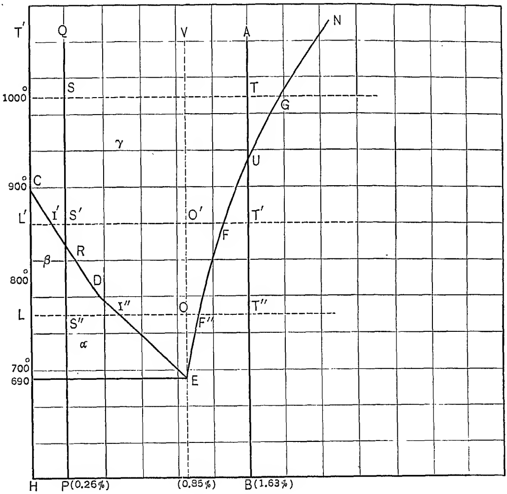

FIG. 47.

What happens when the temperature slowly falls below these limits, that is, below the point corresponding to the intersection of at least one of the two verticals *AB* or *PQ* with the corresponding crystallization curve *EN* and *CE*?

Referring to the case of our first and second experiments the analysis of the successive layers of the specimen quenched at 1000° (Experiment 2) shows us (Fig. 41) that for the cementation carried out with ethylene at 1000° we can apply the method of graphical representation just noted, so that the points of the segment of the line *ST* will represent the concentrations of the carbon and the corresponding depths of the various layers of the cemented zone as long as the temperature remains at 1000°. If, now, we cool the specimen very quickly, we shall "fix," so to speak, this state of affairs; this, precisely, manifests itself in the second experiment. Let us, on the contrary, allow the cylinder to cool very slowly; the representative segment *ST* will then fall parallel to itself in the diagram until first its extreme points and then the points contiguous to these intersect, successively, one of the two crystallization curves *CE* or *EN*, or both. (In the case represented by our drawing, the first curve intersected by the horizontal segment is *EN*.)

From this moment the formation of crystals of ferrite or of cementite begins in the layers which correspond to the points of *ST* which at any instant happen to fall on the intersection of *ST* with either *CE* or *EN*. Thus, in our case, when *ST* is at the height of the point *U*, crystals of cementite begin to form in the layer corresponding to the abscissa of *U* (that is, in the exterior layer of the cylinder); and when the cooling has proceeded a further very small amount, reaching the temperature, for example, corresponding to the value of the ordinates of $S'T'$, cementite will have separated in all the layers corresponding to the points of the segment $F'T'$, and in all these layers the concentration of the carbon still dissolved in the γ-iron will have the value represented by the point F', corresponding to the saturation of the solid solution at that temperature. A further lowering of the temperature should cause the formation of new crystals of cementite in F'. However, while at this point the solution is still homogeneous, in the points of the segment $F'T'$ contiguous to it exist crystals of cementite already formed, acting as "germs" of crystallization, so that the new crystals of cementite, instead of forming in F' proper, form at points which are more toward the right of the segment $F'T'$.

And since this phenomenon can manifest itself along *EN* during the whole slow cooling from 1000° to 690° (point *E*), there results an "accumulation" of the cementite, and therefore a great increase in the concentration of the carbon, at the points nearest to the line *AB* (that is, in the external layers of the cemented piece), while at the points near the line *EV* the concentration of the carbon remains close to the value corresponding to the abscissa of this line (0.85%), this being the value toward which the concentrations of the successive points F', F'', etc., tend.

The same remarks can be made on the separation of the ferrite, which, beginning to crystallize at the points at which *ST* successively intersects the curve *CDE*, "accumulates" at the points near the line *PQ*, greatly diminishing there (and hence at the deeper points of the cemented zone) the concentration of the carbon.

Granted this, it is clear that when the cooling is very slow, so as to make as complete as possible this kind of "liquation" which gives rise to the accumulation of the cementite at the external edge of the cemented zone and of the ferrite in its deeper layers, and when the cooling is extended below the point

E (690°), there must be a great increase (as compared with the values of the diagram of Fig. 41, which represents the distribution of the carbon at 1000°) in the concentration of the carbon in a zone near the line *AB* and to the left of this, a great decrease in the concentration of the carbon in a zone near *PQ*, but to its right, and, finally, a zone around *EV* in which the carbon has a concentration resulting from the absence of the ferrite and of the cementite (accumulating to left and right, respectively), that is, the concentration of the eutectic pearlite, equal to 0.85%, abscissa of the point *E*.

This is precisely the distribution of the carbon which we have seen characterizes the carburized zones obtained by cementing soft steels with volatile hydrocarbons (ethylene, acetylene, etc.), and letting the cemented pieces cool slowly to ordinary temperature.

I have given most evident examples of this in the preceding pages, such as those which correspond to the micrographs reproduced in Figs. 18, 26 and 38 and to the diagram of Fig. 37.

When, on the contrary, the specimen is not allowed to cool slowly to ordinary temperature but is quenched in cold water at a temperature higher than 690°, a somewhat different distribution of the carbon is obtained.

Thus, for example, by cementing at 1000° and quenching at 750° (as in our first experiment), instead of the central zone of constant concentration (0.85% C), we shall have a zone corresponding to the segment *I''F''* (Fig. 47), in which the concentration of the carbon must still diminish about as in the corresponding zone of the specimen cemented and quenched at 1000° (Experiment 2). This is because the points of the segment *I''F''* have not intersected, in the slow cooling, the crystallization curves *CE* and *EN*. This distribution of the carbon appears most clearly in the specimen obtained in the first experiment; in fact, from the diagram (Fig. 40) is to be seen the great increase (as compared with the diagram of Fig. 41) of the concentration of the carbon in the external regions of the cemented zone, due to the accumulation of the cementite in these regions. In the succeeding region (between 1 mm. and 2.2 mm. in depth, corresponding to the segment *I''F''*) the concentration of the carbon varies considerably more slowly.

In the first experiment the cementation had extended too near to the axis of the steel cylinder to make it possible to remove on the lathe the deeper layers of the cemented zones.

The third experiment, carried out under conditions analogous to the preceding but limiting the length of the cementation to one hour, allows a study of these deeper layers. In the diagram obtained from the analyses of the successive layers of this specimen (see Fig. 42), the accumulation of the cementite in the external layers naturally appears less evident, on account of the greater thinness of the cemented zone, but on the other hand the sudden decrease in the concentration of the carbon in the last and deepest layers of the cemented zone (between 0.8 and 0.9 mm. in depth), which could not be shown in the preceding case, is now seen very clearly; a decrease due (according to what I have just explained) to an "accumulation" of the ferrite toward the "nucleus" of the specimen.

Let us see, now, how we can explain the irregular concentration of the carbon in the fourth experiment (see diagram, Fig. 43). Here we evidently can not attribute the sudden decrease in the concentration of the carbon which manifests itself in the intermediate layers of the cemented zone to phenomena of liquation, because the quenching was carried out at the same temperature as the cementation (800°), and was not preceded by any slow cooling during which liquation could have been produced. The explanation of the phenomenon must, on the contrary, be sought in the fact that the cementation was carried out at a relatively low temperature, and at a temperature during which, noting the initial concentration of the carbon in the specimen subjected to the cementation, the iron of this specimen was still present in the state of β-iron.

A phenomenon entirely analogous, though less marked, is observed in the "concentration-depth" diagrams of the experiments which I have reported on pp. 73 and 74, carried out on a large scale with solid cements at relatively low temperatures (850°–880° C.).

It follows clearly, from the 1st, 2nd and 3rd diagrams of Fig. 21 on p. 75 (which refer to these experiments) that the curve which represents the concentration of the carbon as a function of the depth of the analyzed layers presents at first a portion slightly inclined toward the horizontal, then a portion in which the concentration of the carbon decreases rapidly, and finally a third portion again slightly inclined toward the horizontal. In all these cases the course of the "concentration-depth" curves is easily explained as follows:

At a temperature of 800° the iron of the bar with 0.26% of carbon is in the state of β-iron, or, according to the length of the heating during which the equalization of the concentration of the carbon in the mass of the metal is effected, has passed into the state of γ-iron in the zones containing pearlite at ordinary temperature. At any rate, the carbon dissolves in it only with great slowness. No sooner, however, has the carbon content of the first external layers of the bar increased a little as the cementation proceeds, so as to reach the value at which the iron passes from the state of β-iron into γ-iron (which is known to occur at about 800° for 0.3–0.4% of carbon), than these layers begin to cement rapidly. Thereafter the concentration of the carbon in these increases rapidly, while in the contiguous layers, in which the iron has not yet completely passed into the γ-state, the cementation proceeds with the original slowness as long as in these, too, the concentration of the carbon has not reached the value 0.3%. In this case, therefore, the cementation proceeds as follows: the concentration of the carbon in a given layer first rises very slowly up to the value 0.3–0.4%, then increasing rapidly as soon as this value is reached. Thus there must always manifest itself a large difference in the concentration of the carbon between the last layer in which it has reached the value 0.3–0.4% and has thereafter rapidly increased, and the succeeding layer, in which this value has not yet been reached. This is precisely the sudden variation in concentration which is observed in the diagram of Fig. 43.

We must therefore recognize that the causes of the sudden variations in the concentration of the carbon in the cemented zones belong to two distinct groups of phenomena. The first, which manifest themselves when intense cementation is effected at a high temperature, and the cemented pieces are allowed to cool slowly through a more or less wide interval of temperature before quenching them, consist of a true "liquation" of the cementite and of the ferrite during their segregation from the iron-carbon solid solutions. The others, which manifest themselves when the cementation is effected at temperatures below 900° or, more generally, below the point Ar_3 of the steel subjected to the cementation, are due to the varying solubility of the carbon in the three allotropic modifications of the iron.

It is easy to understand, then, why the discontinuities in the distribution of the carbon in the cemented zones are considerably less marked in very deep cemented zones than in thin ones. Thus, for discontinuities of the first class, due to the liquation of the cementite and of the ferrite, we have already seen that the pearlitic zone—their most characteristic feature—does not occupy, in general, more than 1 mm., so that it does not appear clearly if layers thicker than 0.3 mm. are analyzed; and the 5th, 6th and 7th diagrams of Fig. 21 show that this feature does not manifest itself appreciably in the "concentration-depth" curves traced on the basis of analyses of layers several millimeters thick, obtained from cemented zones deeper than 10–15 mm.

The 4th diagram (cementation of 360 hours at 850°-880°) of the same Fig. 21 shows next that the discontinuities due to the second class of phenomena (cementations carried out below 900° C.) also appear but slightly in very deep cemented zones.

The causes of the sudden variations in the concentration of the carbon in the cemented zones having been determined, it was interesting to study the ways of preventing them in order to avoid the phenomena of brittleness connected with them.

The elimination of a first series of discontinuities—those due to the liquation of the cementite—can evidently be obtained by carrying out the cementation in such a way as to avoid the formation of a hyper-eutectic layer containing free cementite. We have already seen on pp. 84–85 that this result can be obtained by carrying out the cementation with carbon monoxide mixed with definite quantities of gaseous hydrocarbons and working under definite conditions of temperature and of pressure.

Experiments 5, 6 and 7 of the table on p. 99, the results of which are reported in the diagrams of Figs. 44, 45, and 46, show the results which can be obtained in this way.

Experiment 6, in which quenching at 1000° (the temperature at which the cementation is effected) "fixes," so to speak, the distribution of the carbon due to the cementation before it is modified by other succeeding phenomena, shows how, by working under the conditions described (of temperature, of pressure and of composition of the gaseous mixture), the hyper-eutectic zone is entirely avoided. And Experiment 5 shows how, the hyper-eutectic zone being absent, the highly supercarburized layer formed in the first experiment is no longer formed during the slow cooling from 1000° to 750°, thus confirming again the correctness of the views set forth.

In Experiment 7 (cementation at 800° and quenching at the same temperature) is seen again the same sudden variation in the concentration of the carbon in the last layers of the cemented zone which manifested itself in 4, carried out under the same conditions of temperature, both as regards the cementation and the quenching.

This confirms still better what we then stated, *viz.*, that this phenomenon is due to the fact that the cementation was effected at a temperature at which the iron of the specimen was still—at least partially—in the state of β-iron.

I have already said that the coincidence of the surfaces of fracture of cemented steels with the surfaces of separation between layers of different carbon content is proved from a very large number of observations analogous to those which I have cited in the preceding pages (see pp. 90–95).[1]

But, even aside from such observations, it is easy to find a reason for this coincidence. In fact, it is known that there is a point of variation in carbon content in a hardened steel corresponding to a variation, equally sudden, of the hardness and of the other mechanical properties, and hence a point of lesser resistance to mechanical forces, due to the different mechanical properties of the two qualities of steel which meet there. The phenomenon manifests itself most acutely over the surface of junction between the eutectic zone and the hypo-eutectic zone when the concentration of the carbon in the latter falls suddenly below the minimum value necessary for the steel to "harden," which is exactly what often occurs in practice, ordinary cemented steels hardening at temperatures between 750° and 800°. In this case the eutectic zone (together with the hyper-eutectic zone) becomes hard and relatively brittle, while the hypo-eutectic zone lying beneath remains tough and easily deformable. It is easy to understand then how the first zone, forming, so to speak, a "brittle crust," sharply separated from the much more malleable nucleus lying beneath, must easily break under the action of mechanical forces which produce in the nucleus a deformation which the "crust" can not follow on account of its hardness and rigidity. The "crust" must then break and "flake off" from the nucleus, which is exactly what characterizes the phenomenon of exfoliation.

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[1] An interesting example of this coincidence of the zone of separation between the hyper-eutectic layer and the eutectic layer is cited and illustrated by a micrograph (without, however, an explanation of the cause) in the work of Bannister and Lambert to which I have already referred (*Journ. of the Iron and Steel Institute*, 1907, Vol. III, p. 117).

At the surface of junction between the hyper-eutectic zone and the eutectic zone the phenomenon of exfoliation under the action of mechanical forces is less intense, because the differences between the mechanical properties assumed as the result of the quenching of the steels constituting the two zones are not so great. In fact, both of these steels harden under the same conditions as cemented steels ; there enters into play only the different "intensities" of this hardening, due to the different carburizations of the two steels and the different variations in volume which the two differently carburized zones undergo as the result of the hardening. This last phenomenon is the cause of the well-known "internal tensions," to which "hardening cracks" are due.

In the exfoliation of the hyper-eutectic zone, however, there enters into action another cause of brittleness, consisting in the scales of cementite which, being quite thick under the conditions which prevail in practice, do not pass completely into the state of solid solution during the heating which precedes the hardening and, remaining even after the hardening in the hyper-eutectic zone, render the latter much more brittle than the eutectic zone lying beneath, which does not contain crystals of primary cementite. This is another important cause of exfoliation "by difference of concentration of carbon."[1]

Granted this, it was evident that the best proof of the correctness of all the theories set forth consisted in cementing and hardening specimens of soft steel under various conditions where the experiments reported in the preceding pages show that the phenomena of exfoliation manifest themselves; also in verifying whether these phenomena are really produced always and only under the circumstances stated. A series of experiments carried out along these lines has fully confirmed the predictions. The results are set forth in detail in the last part of the paper which I have just been considering, but it seems superfluous to me to summarize them here.

As conclusions from the observations and the considerations reviewed in the preceding pages, we can then formulate two general rules to avoid, or at least to reduce, in the cemented and hardened zones, the sudden variations in the concentration of the carbon to which are due the phenomena of exfoliation:

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[1] We have seen (see p. 51) how Guillet had already pointed out the great practical importance of this fact. He had, however, not taken into account the still more important effects of the liquation of the cementite.

1. Avoid effecting the cementation at too low a temperature and, in any case, cement at a temperature higher than that of the point Ar_3 of the steel used.

2. Avoid slow cooling after the cementation and before the quenching.

The first rule is simple and precise and does not require more detailed explanation. Some remarks on the second, however, seem opportune.

It is well known that in the practice generally followed in works for surface cementation of machine pieces, or case-hardening, there is always a slow cooling of the cemented pieces, starting from the temperature of the cementation and before the quenching. In fact, aside from the method adopted in many works of letting the cemented pieces slowly cool in the cementation boxes themselves, then heating them again in salt or lead baths to the hardening temperature, slow cooling ordinarily occurs during the time necessary to withdraw the cementation boxes from the furnace and remove from them one by one the cemented pieces in order to harden them; and, in fact, with a slowness amply sufficient to produce the phenomena of liquation which we have studied.

We shall see later how, in the majority of cases, the disadvantages just mentioned can be avoided by means of a "double quenching," executing the first in water or oil at a temperature but slightly different from that of the cementation. This can be done very easily, especially when the cementation is not effected in the usual boxes but with mixed cements in fixed cementation chambers. The second quenching is performed after having brought the pieces by the usual salt or lead bath to the temperature suitable for final quenching.

Finally, it is evident (and we shall see that experiment fully confirms it) that the sudden variations in the concentration of the carbon produced by the phenomena of the liquation of the cementite and of the ferrite must be the more marked the more rapid the variation of the concentration of the carbon in the cemented zone, before the slow cooling which precedes the quenching, and as long as the temperature remains about constant during the cementation.

In fact, as we have seen, these sudden variations in the concentration of the carbon are, so to speak, but an "exaggeration, localized in definite layers," of the continuous and uniform variation of this concentration which manifests itself before the slow cooling, in the cemented zones, at temperatures higher than the point Ar_3 of the steel used.

The importance of working so as to obtain cemented zones in which, before the cooling, the concentration of the carbon decreases as slowly as possible from the external layers to the deeper ones is therefore evident; in this way the effects of the sudden variations in this concentration which may be produced afterward by the liquation of the cementite and of the ferrite will be reduced to a minimum.

ing out the cementation under definite conditions with carbon monoxide, pure or mixed with small quantities of hydrocarbons, and the results of the experiments collected in the table on page 99 show the efficacy of such methods (see summary and discussion on pages 107–109).

We shall see later how the use of cements based on the special cementing action characteristic of carbon monoxide may find, for the same reasons, useful practical applications. Moreover, we shall see that the use of cements of this class makes it possible to avoid the formation of hyper-eutectic zones, with their dangerous brittleness, in cases in which it is not necessary to obtain extraordinary hardness on the surface of the cemented pieces, such as is very rarely required in practice.[1]

The practical importance of the facts to which I have just referred is shown by the value attributed by experts to cements which they call "gradual," as compared with "violent" cements. This distinction, which experts make from purely empirical data and without knowing the reasons for it, finds its exact explanation in the considerations which I have set forth and which permit of proceeding more rationally in the choice of cements and of the most suitable conditions for their use.

In the meantime, in May, 1909, Charpy published another memoir[2] on cementation, in which, together with a few new experiments, he reviews many of his preceding experimental researches and gives many remarks on the behavior of carbon monoxide in cementation. This paper contains very little new material, and gives the impression of being written chiefly for practical purposes.

Charpy, after having pointed out how he had shown in 1903 that carbon monoxide cements iron, begins by examining the results of the experimental investigations on the same subject preceding his, and dilates especially on the polemic between Caron and Margueritte (of which I have already spoken in Chapter I). He tries to explain by various arguments (some of them not entirely exact) the causes of the false deductions which Caron had drawn from his experiments, both as regards the carburizing action of carbon monoxide on iron and as regards the supposed necessity of the intervention of alkali cyanides in industrial cementation.

In the second part, Charpy repeats the account of previous experiments, which I have already summarized on p. 45, *viz.*, those consisting in cementing pieces of wire and filings of soft steel at various temperatures, in a current of pure carbon monoxide.

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[1] We shall see that in practice it can be useful to obtain concentrations of carbon higher than 0.9% only in certain special types of very thin cemented zones, the use of which is limited to rare cases of little importance. In the very large majority of practical cases, a maximum concentration of 0.9% gives a hardness (after quenching) which is amply sufficient and sometimes even excessive. In Part II of this volume we shall see that devices which permit of lowering the maximum concentration of the carbon in the cemented zones below 0.9% are sometimes useful in practice.

[2] G. Charpy, *Sur la cémentation du fer et de ses alliages par l'oxyde de carbone* (*Revue de Métallurgie*, May, 1909, Vol. VI, pp. 505–518).

The author, however, reports two new experiments, in which he subjected to the action of carbon monoxide soft steel in the form of cylinders 10 mm. in diameter, then determined the carbon in two concentric layers 1 mm. thick. Although this evidently does not allow him to draw any conclusion as to the *distribution* of the carbon in the cemented zone (as follows clearly from what I have said relative to my experiments of the preceding year[1]), it at least furnishes him some information regarding the *concentration* of the carbon.

In the specimen cemented *for* 60 *hours* at 1000° in a "slow" current of carbon monoxide,[2] the external layer contained 0.63% of carbon, while the second layer contained but 0.5%. On the other hand, the external layer of an identical specimen, cemented under identical conditions but without allowing the carbon monoxide to "circulate," contained only 0.20% of carbon; the second layer of this specimen contained 0.15% of carbon; while the original metal contained 0.12%.

It is clear that these last experiments, with the few conclusions which can be drawn from them, cover but a very small part of those published in the preceding year by me and my collaborators; which latter, being supplemented by analyses of many thin successive layers of each cemented zone, had already led to useful conclusions on the operation of the cementation, especially as concerns a question of capital practical importance—the *distribution* of the carbon in the cemented zones.

In the third part of his memoir, Charpy studies the action of carbon monoxide at high temperatures on various metals and on some special steels. By causing carbon monoxide to react at 1000° and at ordinary pressure on chromium, on ferro-chrome with 88% of chromium, and on manganese, he observed the oxidation of the metal and the simultaneous decomposition of the carbon monoxide, with formation of free carbon.

It is well known that this phenomenon had already been studied exhaustively by Schenck in a series of works published, considerably before Charpy's work, in the *Berichte der deutschen chemischen Gesellschaft.* Schenck had, moreover, shown that this phenomenon manifests itself between limits of temperature and pressure well defined for each metal, and had also shown the precise significance of these limits. I will later offer more precise data on this point—the results of recent experimental investigations.

The experiments performed by Charpy with nickel and with tungsten show that carbon monoxide (at 1000° C. and under ordinary pressure) carburizes the first metal only very slightly, while it carburizes the second strongly. Finally, by making carbon monoxide pass at 1000° over filings of various chromium steels or chromium-nickel steels of different composition, Charpy observes that, contrary to what he has shown to occur with iron,[1] the data relative to the carburization of the metal, deduced on the basis of the increase in weight of the filings, of the analysis of the metal and of the evolution of carbon dioxide, are here so different as to show that a considerable proportion of the carbon monoxide oxidizes the chromium. If, instead of using chrome-steel in the form of filings, pieces of considerable dimensions are used, the oxidation of the chromium is limited to the surface layer, while below this the cementation proceeds regularly by diffusion.

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[1] I have already shown (see p. 95) the necessity of analyzing layers not thicker than 0.1–0.2 mm.

[2] Charpy does not indicate the velocity of the current of carbon monoxide, on which, however, the concentration of the carbon in the cemented zone essentially depends.

These results, of themselves incomplete and inconclusive, show clearly that a complete study of the cementation of special steels, carried out along the theoretical lines so clearly developed by Schenck, would without doubt furnish results of great practical interest.[2]

In the fourth part of his memoir, Charpy reports the results of some cementation experiments carried out on a large scale with three of the cements most frequently used in practice: wood charcoal, a mixture of wood charcoal and barium carbonate, and animal charcoal. He did not in these observe the formation of the slightest traces of cyanides, either in the gases or in the solid materials taken from the cementation boxes. This confirms the results of the earlier experiments published in 1865 by Cailletet (see p. 23). Only with the intimate mixture of carbon and barium carbonate do cyanides begin to appear, at about 1050°, but the cementation is already intense at considerably lower temperatures (900°–1000°).

Charpy shows, moreover, that the cementation is somewhat more intense when wood charcoal is used as cement in an atmosphere of carbon monoxide than when it is employed in the presence of its own occluded air. The first precludes the formation of cyanides which, in the second, might be formed (according to the hypothesis of Caron) merely by the action of the nitrogen of the air.

These experiments show that cyanides are not necessary for cementation, and that under the conditions under which cementation is ordinarily effected "the transport of the carbon to the metal is effected, at least for the most part, by the action of the carbon monoxide." The author adds that all the observations of Caron on the influence of alkalis on cementation with wood charcoal are explained just as well by the intervention of carbon monoxide as by that of cyanides. This last assertion has been confirmed by other, considerably more direct, experiments, but not all of the other remarks made by Charpy on this subject are correct.

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[1] See p. 45.

[2] Such a study, evidently very long and difficult, I began a couple of years ago, as I have had occasion to announce in various publications. A part of the first results has already been published, and will be given briefly in the following pages; others will be published shortly, but I of course make no pretense of exhausting so vast a subject.

About two months later I sent to the Editor of the *Gazzetta Chimica Italiana* a paper[1] containing the results of three series of investigations, carried out in collaboration with Doctor Astorri, designed to determine with great precision the specific action of carburizing gases and the way in which this action "adds itself" to that of the solid cements or of those cements (such as ethylene) which, although gaseous, owe their carburizing action essentially to the solid carbon which is formed by their decomposition in contact with the iron.

The first of these series of investigations comprises various cementations carried out under conditions analogous to those described in the preceding papers, using as cement carbon monoxide mixed with benzene vapor in various well-defined proportions.

The experimental conditions adopted in the various tests, together with the results obtained, are shown in the table which follows, as also data relative to the concentration and distribution of the carbon in the cemented zones.

Number	Temperature °C.	Length of cementation (hours)	Quantity and composition of gaseous cement used: gaseous CO (liters) and liquid benzene (c.c.)	Thickness of the zone			Remarks
				Hyper-eutectic (mm.)	Eutectic (mm.)	Hypo-eutectic (mm.)	
1	1000	4.0	6 liters CO 2 c.c. C_6H_6	0.2	0.6	0.2	Slight deposit of carbon on the steel. Concentration of C in hyper-eutectic zone, 1.1%.
2	1000	4.0	6 liters CO 1 c.c. C_6H_6	....	0.7	0.5	No deposit of carbon on the steel.
3	1000	4.0	6 liters CO 1.5 c.c. C_6H_6	0.2	0.6	0.2	Very slight deposit of carbon. Concentration of C in hyper-eutectic zone, 1.1%.
4	1000	4.0	6 liters CO 15 c.c. C_6H_6	0.7	0.4	0.4	Abundant deposit of powdery carbon.
5	1000	2.0	3.75 l. CO 19 c.c. C_6H_6	0.7	0.4	0.4	Very abundant deposit of carbon.
6	1000	2.5	19 c.c. C_6H_6	0.7	0.6	0.5	Deposit of compact carbon about 1 mm. thick.

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[1] F. Giolitti and L. Astorri, *Ricerche sulla fabbricazione dell'acciaio cementato*, IV: Sulla funzione specifica dei cementi gassosi e dei cementi solidi nel processo della cementazione (*Gazzetta Chimica Italiana*, 1910, Vol. XL, p. 1).

This Note, sent to the Editor of the *Gazzetta Chimica* July 30th, 1909 (as is seen from the statement printed as subtitle by the Editor), was published only six months later.

These results, compared with those carried out with pure carbon monoxide reported further back, show that the addition of small quantities of volatile hydrocarbons to carbon monoxide merely raises the concentration of the carbon in the external layers of the cemented zones above the value which would result from the use of pure carbon monoxide under identical experimental conditions. This increase is greater the larger the proportion of the hydrocarbon contained in the gaseous mixture, as long as this proportion does not reach a value such that the velocity with which the free carbon is formed by the decomposition of the hydrocarbon does not surpass the velocity with which this carbon passes through the stage of carbon monoxide into solution in the iron. From this limit (about 1.8 c.c. of liquid benzene to six liters of CO) the excess of carbon which is liberated begins to deposit on the steel and the concentration of the carbon in the external layers of the cemented zone reaches the maximum value corresponding to that which is obtained by cementing with solid cements, or with cements which behave as such, and from this point on, the concentration and the distribution of the carbon in the cemented zones no longer vary markedly, even if the proportion of the hydrocarbon increases greatly.

From what precedes it is evidently possible to obtain, by means of mixtures of carbon monoxide and vapors of volatile hydrocarbons, cemented zones in which the maximum concentration of the carbon in the external layers has a definite value, lying between a minimum corresponding to that which would be obtained by working under the given conditions with pure carbon monoxide, and a maximum which would be obtained by working with the vapors of the hydrocarbon alone. This is achieved simply by using gaseous mixtures containing a proper proportion of hydrocarbon varying with the conditions under which the cementation is to be effected, such as temperature, pressure, relation between the velocity of the gaseous current and the surface of the steel to be cemented, etc.

The practical importance of these observations is evident, widening, as they do, the field of application of carbon monoxide in the cementation of steel, and making it posssible to combine the advantages of the use of this gas with those of the other cements and of "graduating" the concentration of the carbon in the cemented zones.

The second series of experiments covers cementation effected by using simultaneously carbon monoxide and wood charcoal.

The steel cylinders were placed, coaxially, in the usual porcelain tube, now set vertically and, together with them, the usual smaller porcelain tube to protect the thermo-electric pyrometer couple. The space still remaining free in the larger tube was filled with a granular wood charcoal, washed with hydrochloric acid and then ignited, using only the portion which passed through a sieve of 49 mesh per sq. cm., and was held by a sieve of 169 mesh per sq. cm.

A current of pure carbon monoxide of definite velocity was admitted at the lower end of the tube.

In the table reproduced below are reported the results of four of the many experiments carried out by this practically important process.

Number	Temperature °C.	Length of cementation (hours)	Volume of CO used (liters)	Thickness of the zone			Remarks
				Hyper-eutectic (mm.)	Eutectic (mm.)	Hypo-eutectic (mm.)	
1	900	4	2	....	0.4	0.9	
2	1000	4	2	....	1.0	0.6	
3	1000	4	6	....	1.0	0.7	
4	1000	4	0	0.7	0.6	0.2	Comparative cementation carried out under the conditions which most frequently manifest themselves in practice: with ordinary wood charcoal, simply ground (not washed nor sifted), and without a current of carbon monoxide.

It appears from the examination of the results of the first three operations, especially if these results are compared with those of the fourth cementation, carried out under the conditions which are usually found in practice, that the characteristic of the cemented zones which are obtained with "granular" carbon in a current of carbon monoxide is the absence of the external hyper-eutectic zone. This characteristic, which we shall see always manifests itself when working within certain limits of temperature, pressure and length of the operation, is easily explained when we take into account the characteristic function of the carbon monoxide as an "equalizer" of the concentration of the carbon in the cemented zones. In fact, as I have already explained, the mixture of carbon monoxide with small quantities of carbon dioxide (in our case, the mixture which is in equilibrium with the free carbon) acts, by its rapid diffusibility, as "carrier" for the carbon which burns at the points of the cemented zone where it is more concentrated, while it again sets it free where the concentration of the latter is smaller; in this way the accumulation of the carbon in the external zones of the steel is impeded.

In other words, in this case also the specific action characteristic of carbon monoxide, as I have previously defined it (p. 87), superposes itself on the specific action of the solid cement, long since known, which follows from the fourth experiment of the table reproduced above, giving a cemented zone of a *type intermediate* between the two which I have described on pages 82 and 84.

Finally, the third series of experiments relates to the study of cementation by pure solid carbon in a vacuum, or in the presence of gases other than carbon monoxide.

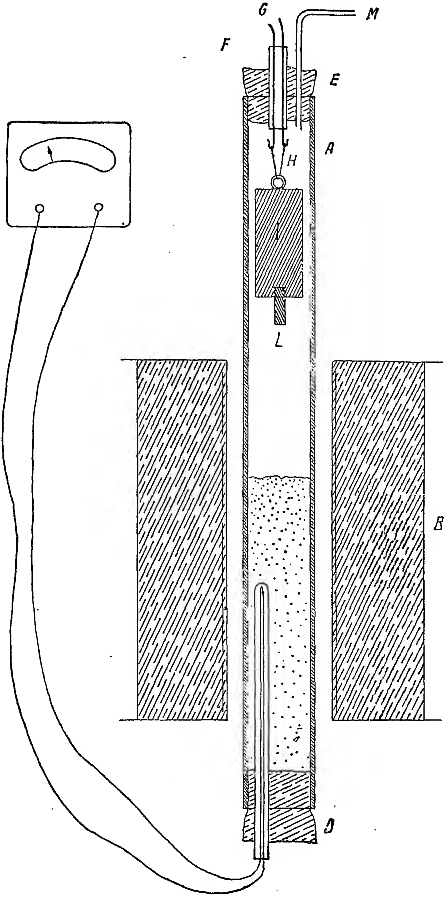

FIG. 48.

For the study of cementation in a vacuum, we adopted, after various unsuccessful attempts, the following experimental arrangement. The usual tube of glazed porcelain (*A*), the Heraeus furnace (*B*) and the Le Chatelier pyrometer with its porcelain protector were arranged as indicated in Fig. 48. In the lower half of the tube we placed the carbon, washed in the way I have already mentioned and reduced to a very fine powder, because the earlier experiments had shown that "granular" carbon does not give sufficient contact with the iron. Through the upper stopper *E* passed, besides the glass tube *M*, a porcelain tube *F*, 15 cm. long, through which ran, from one end to the other, two large copper wires, insulated and fastened in the tube by means of an insulating cement poured into it.

The lower ends of the two wires, bent into a hook, were connected by a fine iron wire, from which was suspended a steel cylinder *I*, 30 mm. in diameter by 150 mm. in height.

In the center of the lower base of this cylinder was bored a threaded hole into which was screwed the cylinder of soft steel *L* (10 mm. in diameter and 30 mm. high), the head of which was likewise threaded. The composition of the steel of the cylinder was as follows:

Carbon	0.09 percent.
Manganese	0.72 percent.
Silicon	traces
Sulphur	0.04 percent.
Phosphorus	0.08 percent.

Having heated to 1100° the lower half of the tube *A*, containing the carbon, while the cylinders *I* and *L* remained in the cold upper part of the apparatus, we produced a vacuum by means of the tube *M*, connected to a mercury pump, until the pressure in the interior of the cementation chamber was permanently reduced to less than 0.5 mm. of mercury. Then we filled the apparatus with pure nitrogen and again evacuated it.

Having repeated the operation three times, in order to be sure of having eliminated the last traces of oxygen which could form carbon monoxide, and keeping the vacuum at less than 0.5 mm. of mercury, we connected for a moment, by means of conductors, each of the external ends of the two copper wires *G* with each of the two electrodes of the furnace; the current which in this way passed through the fine iron wire *H* was sufficient to melt it, and the system of two cylinders *IL* fell on the carbon powder, which was compressed by the base of the cylinder *I*, while the cylinder *L* penetrated into it.

We then kept the temperature constant at 1000° for three hours and a half, during which time, in order to always keep the pressure below 0.5 mm., it was sufficient to work the pump very slowly to remove the very small quantities of air which penetrated at the high temperature through the porcelain walls. These minimum quantities of air have no influence on the process of the cementation. The air leak was due to the slight permeability which the porcelain assumes at a very high temperature, and not to imperfect closing of the connections of the apparatus, as was proved by the fact that when the experiment was finished the external pressure no longer increased (from 0.4 mm.) during the twelve succeeding hours in which the cold apparatus was allowed to stand without working the pump.

Having removed the steel from the tube, we noted that carbon adhered to the whole surface of the smaller cylinder, except the last half centimeter, and to the bottom of the large cylinder, forming a friable crust half a centimeter thick, an evident proof of immediate contact.

Fig. 49.

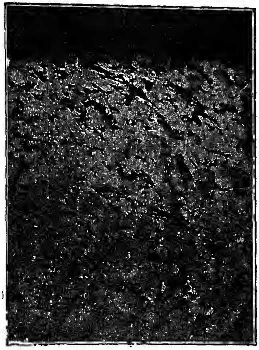

Fig. 50.

On examining under a microscope the section corresponding to the point at which the carbon did not adhere, we could detect no increase in the proportion of pearlite toward the external edge; this is plainly evident in the photogram of Fig. 49.

If, instead, the sample was cut at one of the points at which the carbon had adhered, and examined in the same way, we noted an appreciable cementation, as appears in the photogram of Fig. 50.

The cemented zone, hypo-eutectic but considerably richer in pearlite than the original steel before the operation (see the deep zones in Fig. 49), is uniform along the whole external edge partially reprodūced in Fig. 50, and has a thickness of about 0.15 mm.

These observations confirm fully what I had asserted before, that solid carbon also, heated above 800° in contact with iron, dissolves in it, cementi it, even without the intervention of gaseous substances.

In fact, if the cementation, observed in our last experiment only at th points at which the solid carbon had come into direct contact with the surfa of the iron, had been due to the intervention of the small quantities of g which the action of the mercury pump had not succeeded in eliminating, tl cementation ought to have been produced in the contiguous zones al: that this did not occur is proof that the very small quantities of gases maining in the tube exercised no appreciable action, while the solid carb exercised such an action directly, as was shown by its "localization" at t points in most intimate contact with the carbon.

From the present experiments, and from those described before, it follo that although gaseous cements have a preponderant action in the proce of cementation, solid carbon also, when it is in intimate contact with β-ir and with γ-iron, dissolves in it, cementing it. And it is quite probat that the results apparently contradicting this assertion, obtained pr viously by some experimenters (for example, by Guillet; see p. 63), a due to the lack of sufficiently intimate contact between the iron and tl carbon.

We used the same apparatus, just described, to investigate the cour of the cementation by solid carbon and pure nitrogen, adding through tl lower stopper *D* a second glass tube through which we admitted nitroge The carbon was the same as that used in the preceding experiments.

The pure nitrogen (prepared from ammonium nitrite) passed through drying apparatus and a glass tube 40 cm. long containing metallic copp heated to redness, to eliminate oxygen completely, before reaching tl cementation chamber.

The cementation apparatus was first emptied of air and then filled wit nitrogen, the same operation being repeated several times; finally, havir again evacuated it, we brought it to 1000° C., keeping in it for about a hour the minimum obtainable pressure (about 0.4 mm. of mercury) to mak sure of having eliminated practically all the gases contained in the tube an occluded in the carbon. We then filled the apparatus with nitrogen an connected the exit tube *M*, which before communicated with the pump, wit a mercury valve so as to prevent the possibility of the entrance of air int the apparatus owing to a diminution in the volume of the gas due to accident cooling.

Having done this, we allowed the two cylinders of steel to fall upon th carbon and began to circulate nitrogen through the apparatus. The ten perature was kept constant at 1000° C. for four hours, during which 2.5 liter of nitrogen passed through.

We obtained in this way a cemented zone which, as appears from th photogram reproduced in Fig. 51, is entirely similar to those which are ob tained by cementing with pure carbon monoxide at 1000° C.[1]; it consists, in fact, of a single hypo-eutectic layer 1.8 mm. deep, in which the concentration of the carbon does not surpass, even at the external edge, the value 0.3%, then decreasing slowly and continuously toward the interior, finally reaching (at a depth greater than 1.8 mm.) the value which it had in the original steel. The photogram of Fig. 52 represents the center of the section examined.

The results of this experiment do not confirm those obtained by other experimenters (for example, by Guillet; see p. 49), showing, on the contrary, that the carburization which is obtained by making nitrogen act on iron at a high temperature in the presence of solid carbon must be due to a reaction analogous to that on which is based the cementation by means of carbon monoxide. And here, too, there must be reached a state of equilibrium, as occurs with carbon monoxide, defined not only by the partial pressures of the various gases in the carburizing atmosphere which is formed by the said reactions, but also by the concentration of the carbon in the γ-iron of the cemented zone.

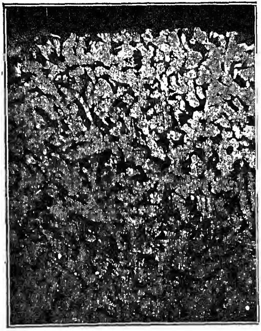

FIG. 51.

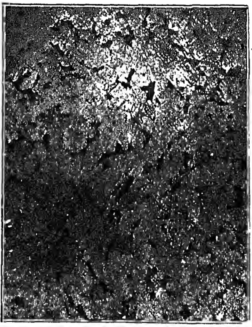

FIG. 52.

The note which I have just reviewed, although presented to the editor of the *Gazzetta Chimica Italiana* on July 30, 1909 (as seen from the subtitle added by the editor and from the fact that this work was presented by Doctor Astorri as a thesis for his doctorate in chemistry, taken at the University of Rome in June, 1909), was not published until six months later. To this delay is due the fact that two other experimenters, Guillet and Griffith, not knowing of the results already obtained by us on cementation with solid carbon in a vacuum, repeated our experiments, although with different experimental arrangements.

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[1] See Fig. 27.

However, the fact that two series of experiments executed absolutely independently gave identical results is the best proof of the correctness of these results.

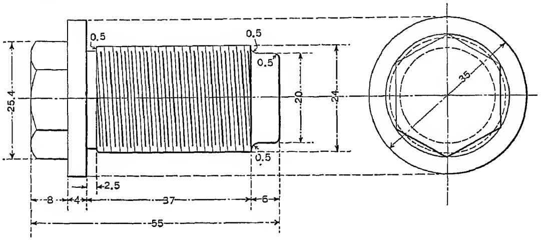

FIG. 53.

A record of the experiments of Guillet and Griffith appears in the October, 1909, number of the *Revue de Métallurgie.*[1] The article begins with a historical review of the question of the intervention of gases in cementation, laying special stress on the discussions between Caron and Margueritte, and between Guillet and Ledebur, of which I have already spoken at length. Then follows a description of the new experimental researches, designed to find whether pure carbon can cement in a vacuum either without pressure or under pressure sufficient to insure contact between the carbon and the iron.

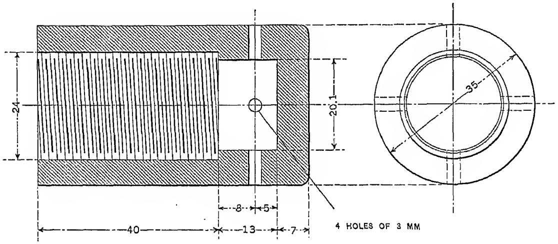

FIG. 54.

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[1] See also the "*Berichte der Abteilung für theoretisches Hüttenwesen*" in the "Proceedings of the Congress of Metallurgy of Düsseldorf" (1910).

The metal used was extra soft steel in the form of wires, sheets and fragments of bars. The carbon (from sugar) had been heated at 1000°, first in a current of chlorine and then in a vacuum. The apparatus (consisting essentially of a long tube of glazed porcelain) was entirely similar to that used by me and Astorri. Guillet and Griffith took (as we did not) the precaution of eliminating the gases from the carbon and from the steel by long iginition in a vacuum, but not that of avoiding (as we did) exposure of the steel and the cement (even for a fraction of a second) to the action of the air or of any gas whatever, before coming in contact with each other.

A first experiment, "without pressure," consisted of igniting iron wires, simply placed in a porcelain boat filled with sugar carbon, in a vacuum for five hours at 1000° C. This did not give rise to the slightest trace of cementation.

A second experiment was carried out by igniting, also at 1000° for five hours, sugar carbon kept in contact with a small plate of soft steel by the pressure of a piece of steel of a few grams in weight. This also gave completely negative results.

Finally, a third series of experiments was carried out by means of the apparatus shown in Figs. 53 and 54. This consists of a hollow steel cylinder closed at one end with a screw plug, which makes it possible to compress strongly the substances contained at the other end of the cylinder, which, closed at the bottom, forms the cementation chamber.

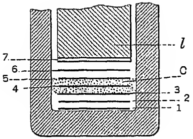

FIG. 55.

The cementation chamber has four lateral holes to allow of its evacuation. The experiments were executed by placing in the cementation chamber sheets of extra soft steel (with 0.08% of carbon), alternating with layers of the usual powdered sugar carbon, as indicated in Fig. 55. A first test was made by heating the apparatus for five hours at 1000° after having tightened the screw plug only very slightly; the concentration of the carbon in the central lamina increased to 0.15%. In a second test, made under conditions identical to those in the preceding one but after having tightened the screw plug as much as possible, so as to strongly compress the carbon against the steel sheets, the concentration of the carbon in the central sheet rose to 0.32%.

As is seen, these experiments confirm my conclusions concerning the possibility of cementing iron with solid carbon without the intervention of gases, and concerning the necessity of an intimate contact between the carbon and the metal in order that such a process may be effected; they further establish the fact that an increase in the pressure which produces such a contact gives rise to an increase in the cementation.

These conclusions, thus formulated by Guillet, have a special probatory value, as with them their author comes practically to a recognition of the incorrectness of his earlier opinion (see p. 63) as to the necessity of the intervention of gases in cementation; this he would not have done if the results of his last experiments had not appeared absolutely unassailable to him.

Weyl, of Aachen, published a paper more than six months after the note of Guillet and Griffith and that by myself and Doctor Astorri,[1] in which are reported with the most minute particulars the results of a large number of experiments carried out with the greatest care and accuracy for the purpose of establishing if pure carbon can cement in a vacuum. It does not seem necessary to review here the memoir of Weyl, as the experiments reported in it are performed along lines absolutely identical with, and with experimental arrangements very similar to (though more perfect than), those forming the subject of the two preceding papers. The conclusion which Weyl draws from his experiments are identical with those formulated by Guillet and Griffith and by me and Astorri. However, there is no doubt that the confirmation of the earlier conclusions by Weyl's experiments, made on materials of exceptional purity and with truly extraordinary accuracy, has great scientific value.

Conclusions contradictory of those of the three last papers were reached by Charpy and Bonnerot.[2] By heating for a long time in as perfect a vacuum as possible, at 1000° C., soft steel in contact with carbon (graphite, diamond or sugar carbon), after first having separately ignited the two substances at 1000° C. for a long time in a vacuum, they were unable to detect the slightest trace of cementation. They conclude that "solid carbon outside of a fragment of steel can not penetrate into it without the intervention of a gaseous vehicle," and they attribute the different results obtained by other experimenters to the insufficient elimination of the gases occluded in the carbon and in the steel used.

However, the decision whether the direct action of the carbon is extremely small (as the experiments of Guillet and Griffith and of myself and Astorri would indicate) or *nil* (as the experiments of Charpy and Bonnerot would seem to show) is a matter which is at most one of theoretical interest. Both series of experiments show with entire certainty that the direct action of the carbon ("by contact"), whether it is *nil* or only very small, is certainly such that it can be considered as *absolutely negligible* in any technical process of cementation.[3] The question thus loses practical interest.

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[1] Fritz Weyl, *Ueber Zementation im luftleeren Raum mittels reinem Kohlenstoff* (*Metallurgie*, July 22, 1910, Vol. VII, pp. 440–456); and "Proceedings of the International Congress of Metallurgy" held at Düsseldorf in June, 1910 (*Berichte der Abteilung für theoretisches Hüttenwesen*, p. 178).

[2] *Comptes Rendus de l'Académie des Sciences*, January 17, 1910, Vol. CL, p. 173.

[3] In either case, the hypotheses of Mannesmann, Roberts-Austen, Ledebur, etc., which attribute the carburizing action of the solid cements used industrially to the *direct* action of the carbon are certainly shown to be false.

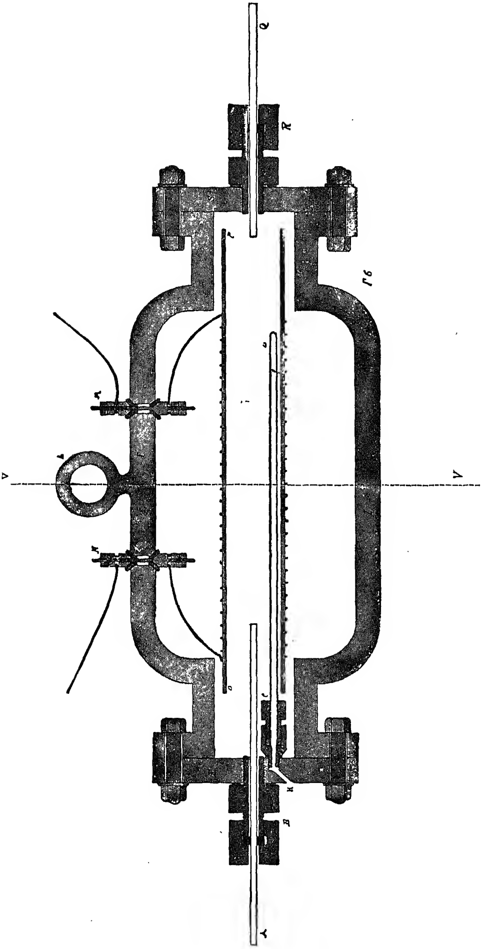

FIG. 56.—(Scale 1:5).

Besides the experiments which I have reported in the preceding pages, the effects which the variations in the pressure of the gases produce in those cases in which free carbon and gaseous cements act simultaneously in the cementation prove clearly the preponderating influence of the gases in the process of cementation, along with a very small direct action of the solid carbon. I have already said something of these effects in connection with one of my first series of experiments on cementation with ethylene,[1] but they come out considerably clearer from another series of investigations carried out in collaboration with Doctor Carnevali and published (although not completely) early in 1910.[2]

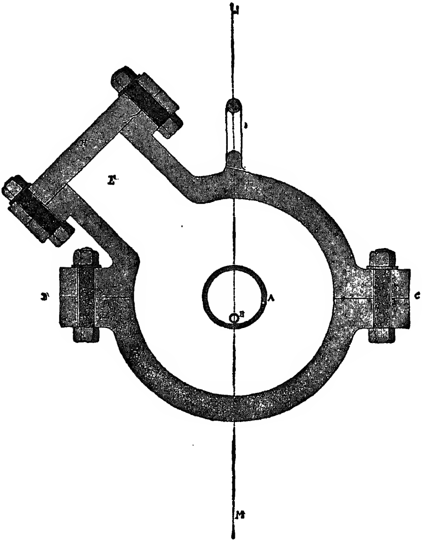

Fig. 57.—(Scale 1:5).

The apparatus which served to effect the cementations with strongly compressed gases (and which we still use, except for slight modifications, in

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[1] See p. 78. We have already seen that in the cementation with ethylene, the gas acts in the presence of solid carbon separating from the first portions of it.

[2] F. Giolitti and F. Carnevali, *Ricerche sulla fabbricazione dell'acciaio cementato*, V: Cementazione con gas fortemente compressi (*Rendiconti della Reale Accademia delle Scienze di Torino*, 1910).

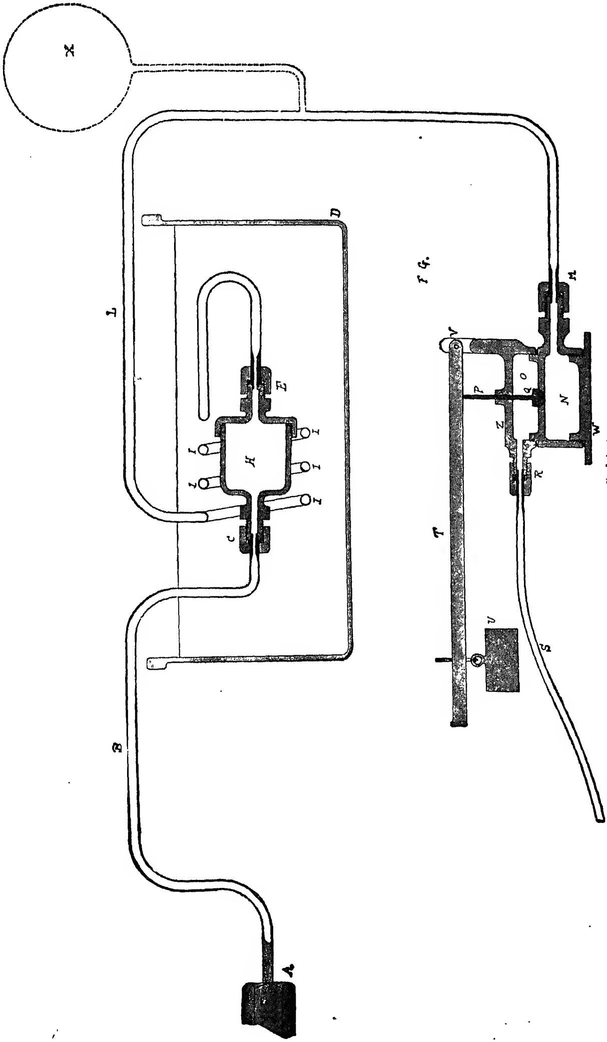

FIG. 58.—(Scale, 1:4).

the continuation of these investigations) is represented in its various parts in section in the three accompanying figures (on a scale of 1:5 and 1:4; see Figs. 56, 57 and 58).

The body of the apparatus is formed of a cylindrical vessel of crucible steel, consisting of two superposed halves fitted to each other by means of a series of screw bolts which allow of strongly drawing together the two well-planed flanges (*C, D*, Fig. 57), between which is interposed a layer of asbestos board saturated with extra dense oil.

The apparatus is prolonged into two cylindrical ends, furnished with planed flanges, on which are fitted two covers *E, S* (Fig. 56), each held by means of eight screw bolts; a good joint is obtained here, also, by means of a layer of asbestos impregnated with oil.

A cylindrical adjunct, identical to the two just described, is provided in the central part of the body of the apparatus (*E*, Fig. 57). This is closed in the same way as the other two, by means of the steel disk *H* (Fig. 57), and its axis is inclined about 45° to the horizontal.

Through the two covers *E* and *S* (Fig. 56) pass two copper tubes of small bore (*A* and *Q*) by means of two screw joints (*B* and *R*) with gas-tight washers. Moreover, the cover *E* has still another hole *H*, communicating by means of a pressure-stopper joint with the interior of the porcelain tube *CD* forming the guard for the thermo-electric couple for measuring the temperature of the interior of the furnace. The two wires of platinum and of rhodium-platinum, insulated from each other by means of the usual porcelain tubes, issue from the apparatus through the hole *H*.

In the apparatus is placed longitudinally the porcelain tube *OP* (Fig. 56), around which is wound in a spiral a nickel wire insulated by wrapping it in asbestos paper and asbestos string; the ends of the wire are joined to two bronze connectors, *N* and *M*, electrically insulated from the body of the apparatus, through which they pass, by means of four fiber cones screwed down on the conical openings of the two holes so as to produce perfect closing. An electrical current of suitable intensity, sent by means of the connectors *M* and *N* through the nickel wire, makes it possible to bring it and the porcelain tube around which it is wound to a temperature which can go as high as 1200° C. and can be kept perfectly constant for many hours.

Having removed the cover *S* (Fig. 56), the pieces to be cemented are introduced into the tube *OP*. In the first series of experiments, of which we are now speaking, we then filled all the space in the tube *OP* still remaining free with granular wood charcoal,[1] washed successively with hydrochloric acid and water and ignited for a long time at about 1300° C. The charcoal was held in the tube by means of two asbestos plugs. Having closed the cover *S* (Fig. 56), the two connectors *N* and *M* were set in place, the hand

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[1] Passed through a sieve of 16 mesh to the sq. cm. and held on a sieve of 81 mesh to the sq. cm.

and the key being introduced through the opening *E* (Fig. 57); by means of this same opening, all the space between the porcelain tube and the steel wall was filled with asbestos fiber so as to protect the latter from the effect of the high temperature to which the porcelain tube must be raised. Finally the cover *H* was replaced, the bolts being well tightened.

Having connected the tube *A* with the vessel containing the compressed gas, this is let into the apparatus, circulates through it from one end to the other, and issues through the tube *Q* (Fig. 56).

The copper tube *Q* (Fig. 56), through which the gas issues from the furnace, is connected with an apparatus which regulates the pressure, represented in section in Fig. 58 (scale, 1: 4). This apparatus consists of a bronze chamber *H*, in which the slowing of the gaseous current owing to the widening of the section and the cooling obtained by means of a bath of running water *D*, condense the less volatile substances which are sometimes formed in large quantities, as when the vapors of certain heavy hydrocarbons are used as cements. The gases having been further cooled in the copper tubing spiral *I*, *I*, penetrate into the bronze box *N*, from which they can issue only by raising the polished bronze valve *Q*, weighted by means of the weight *U* sliding on the lever *T*. Along the course of the tube *L*, connecting the refrigerating apparatus with the box *N*, a manometer is inserted by means of a small copper tube, schematically indicated by *X* in Fig. 58. The washers of the various screw joints were made of rings of pure tin.

I report a single one of the series of experiments carried out with the apparatus just described, working at different temperatures and pressures and using various carburizing gases, *viz.*, cementations effected at 1100° C., using carbon dioxide under different pressures in the presence of granular carbon prepared in the way I have already described. Various experiments showed that carbon dioxide reacts with carbon at 1100° C. with such velocity that it is sufficient that the carbon dioxide, passing in quantity of 15 to 20 liters per hour, should traverse a layer of granular carbon only 6–7 cm. thick before arriving at the steel cylinders, to insure that the conditions of equilibrium of the two gases with free carbon at the given temperature shall have been reached. We can therefore practically consider that, knowing the concentrations at equilibrium of the two gases at 1100° C., the cementations of our first series are effected as if we had used carbon monoxide directly instead of carbon dioxide. Assuming this, the following table gives the results of the first series of experiments,[1] carried out with steel cylinders of the following composition:

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[1] The thicknesses indicated for the various zones are the mean of micrometric measurements made at many points of each specimen and not differing from each other by more than 0.05 mm. The thickness of the hypo-eutectic zones is measured from the point where the edges of primary cementite begin to the point where the concentration of the carbon is reduced to about 0.3%; there is possible, therefore, in this group of zones, an error of even 0.1 mm.

Carbon	0.14 percent.
Manganese	0.80 percent.
Silicon	0.03 percent.
Sulphur	0.05 percent.
Phosphorus	0.02 percent.

Number	Temperature	Pressure (kg. sq. cm.)	Time of cementation (hours)	Thickness of hyper-eutectic zone (mm.)	Thickness of eutectic zone (mm.)	Thickness of hypo-eutectic zone (mm.)	Total thickness of cemented zone (mm.)
1	1100° C.	9.5	2	1.3	0.6	1.2	3.1
2	1100° C.	ord. press.	2	0.0	0.5	1.1	1.6
3	1100° C.	15.0	1	0.8	0.7	1.0	2.5
4	1100° C.	6.0	7	2.0	1.1	2.0	5.1
5	1100° C.	ord. press.	7	0.0	1.6	1.8	3.4

The table at once clearly places in evidence the marked effect of the pressure of the cementing gas on both the velocity of the cementation and the concentration of the carbon in the cemented zones.

As regards the first point—the velocity of the diffusion of the carbon into the steel—it is enough to compare the results of the first experiment with those of the second to see how, all other conditions remaining constant, the increase in pressure from one to over nine atmospheres almost doubles the total thickness of the cemented zone obtained in two hours, raising it from 1.6 mm. to 3.1 mm.

The fourth and fifth experiments show that for a cementation of seven hours at 1100° C. the increase in pressure from one up to six atmospheres increases the total thickness of the cemented zone in the ratio of 3 to 2 (from 3.4 mm. to 5.1 mm.).

Finally, a comparison of the third experiment with the second shows that working at ordinary pressure it takes two hours to obtain a cemented zone whose thickness is less than two-thirds of that which can be obtained in one hour under a pressure of 15 kg. per sq. cm.

The effect of the pressure of the gas on the concentration of the carbon in the cemented zones follows clearly from a comparison of the first experiment with the second and of the fourth with the fifth. These comparisons show that while in the cemented zones obtained at ordinary pressure the hyper-eutectic zone is missing and the concentration of the carbon can not therefore exceed in them 0.9%, the zones obtained by cementation at pressures between 6 and 9.5 kg. per sq. cm. always contain well-developed hyper-eutectic zones.

It is self-evident that the strong influence which the pressure of the carburizing gas exercises on the depth of the cementation and on the concentration of the carbon in the cemented zones, while solid carbon is simultaneously present, is a sure proof of the preponderating activity of the gas in the cementation process over that of the solid carbon.

Moreover, a further proof of the diffusion of the carburizing gases into the mass of the steel during the process of cementation is furnished by a comparative study of the cementation of steels of different original content of carbon. I reported several series of experiments of this nature, carried out in collaboration with Dr. Carnevali, in a paper published at the beginning of 1910.[1] The following table gives one of these series, carried out by cementing for three hours, at 1100° C., but with various cements, two steels of the following composition:

	Steel A	Steel B
Carbon	0.18 percent.	0.94 percent.
Manganese	0.35 percent.	0.90 percent.
Silicon	0.05 percent.	0.17 percent.
Phosphorus	0.07 percent.	0.04 percent.
Sulphur	0.05 percent.	0.02 percent.

The following table shows that the cemented zones, all other conditions being equal, are deeper the higher the carbon content of the steel used.[2] It is clear that the contrary should manifest itself if the cementation were

Number	Cementing gas	Pressure (mm.)	Steel A				Steel B	Quantity of gas passed during 3 hours into cementation chamber (liters)
			Thickness of hyper-eutectic zone (mm.)	Thickness of eutectic zone (mm.)	Thickness of hypo-eutectic zone (mm.)	Sum of the three thicknesses (mm.)	Thickness of hyper-eutectic zone (mm.)	
1	Ethylene...	760	1.8	0.6	0.4	2.8	4.7	5
2	Ethylene...	458	0.9	0.4	0.4	1.7	2.6	5
3	Methane...	757	1.5	0.5	0.5	2.5	3.2	5
4	Methane...	463	1.1	0.4	0.3	1.8	3.1	5
5	Carbon monoxide[3]	762	....	....	3.2	3.2	4.1	5
6	Carbon monoxide	461	....	....	3.0	3.0	3.8	5
7	Ethylene...	762	0.8	0.5	0.4	1.7	2.4	1
8	Ethylene...	759	1.9	0.6	0.5	3.0	4.5	15

[1] F. Giolitti and F. Carnevali, *Ricerche sulla fabbricazione dell'acciaio cementato*, VI: Cementazione di acciai ad alto tenore di carbonio, con gas alla pressione atmosferica e a pressione ridotta (*Rend. della Reale Accademia delle Scienze di Torino*, 1910).

[2] I call attention to the fact that this result does not harmonize with those obtained a few years before by Guillet (see p. 47).

[3] The increase in the concentration of the carbon which is obtained by cementing with carbon monoxide at temperatures higher than 1000° C. is quite small (see *Gazz. Chim.* 1908, p. 341, *et seq.*).

In these cementations, small quantities of carbon dioxide (0.5–0.2%) mixed with the carbon monoxide are sufficient to "invert" the reaction, substituting a process of refining for that of cementation. Such an inversion is evidently impossible in cementations carried out with hydrocarbons.

effected without the intervention of the diffusion of the gases but by simple carbon diffusion "by difference in concentration" of the carbon dissolved by direct contact in the surface layers of the steel.

The high concentrations of carbon in the cemented zones which are obtained by starting from steels of considerably high carbon content (such, for example, as the steel *B* above) greatly accentuate the phenomenon of liquation of the cementite, the practical importance of which I have already referred to.[1] The study of the phenomenon in this special case confirms fully the conclusions drawn from the earlier experiments.

As an example of the importance which the phenomenon of liquation of the cementite may attain, I reproduce in Fig. 59 the micrograph[2] of the edge of a cylinder of the steel *B*, cemented with methane for three hours at 1100° C. and allowed to cool slowly in the furnace. The great quantity of cementite is clearly seen, accumulated (necessarily as the result of liquation) in the deeper parts of the cemented zone, and leaving *at the periphery* a zone more than a millimeter thick in which the concentration of the carbon does not exceed the value which it originally had in the steel used.

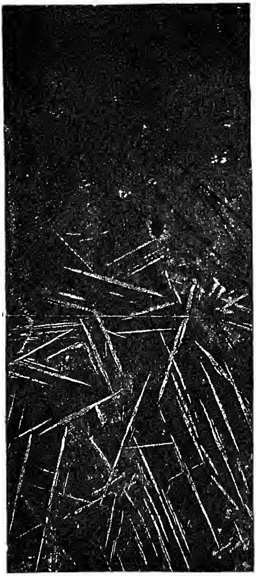

Fig. 59.

We have thus demonstrated the great practical importance of any means which allows of obtaining cemented zones in which the concentration of the carbon does not exceed 0.9% in the surface layers, and varies from these to the deeper layers as slowly and uniformly as possible. These belong to that "*intermediate type*" which we have defined by referring to the two characteristic types which are obtained by cementing with pure carbon monoxide and with pure ethylene (see p. 82). We have also seen (see p. 108) that the simplest of these means consists in properly utilizing the characteristic carburizing action of carbon monoxide, increasing by means of the addition of other carburizing substances, such as hydrocarbons or solid carbon, the too low concentration of carbon which would otherwise be obtained, under ordinary conditions of temperature and pressure.

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[1] See p. 93.

[2] Enlargement 50 diameters. Etched with picric acid in alcoholic solution.

The importance of an accurate study of the processes of cementation based on the specific action of carbon monoxide is thus made evident. The practical results of such studies and their industrial applications are set forth in the second part of this volume; for the present, I report only the results of some laboratory experiments designed to define precisely the course of cementation effected with carbon monoxide in the presence of free carbon The results of these studies, which I carried out in collaboration with Doctor Tavanti, are collected in a paper published early in 1910.[1]

The experiments whose results I report were carried out with the usual experimental arrangement already described (see pp. 96 and 116), using cylinders 18 mm. in diameter by 150 in length, of soft steel of the following composition:

Carbon	0.14 percent.
Silicon	0.03 percent.
Manganese	0.80 percent.
Sulphur	0.05 percent.
Phosphorus	0.02 percent.

The wood charcoal was ground and washed in the usual way, and we used the portion passing through a sieve of 16 mesh per sq. cm. and retained by a sieve of 81 mesh per sq. cm. Instead of carbon monoxide we used carbon dioxide, after having ascertained, by means of some preliminary experiments, that the gaseous mixture of CO and CO_2 resulting from the action of the carbon dioxide on the front layers of carbon had really reached the composition corresponding to complete equilibrium with free carbon. The experiments showed that these conditions of equilibrium are attained when the gaseous mixture has traversed a layer of granular carbon 25 cm. thick, even when giving to the current of gas a velocity (1 liter in 9 minutes) more than four times that used in our cementation tests (1 liter in 40 minutes). Besides its obvious practical advantages, the use of carbon dioxide is preferable to the direct use of pure carbon monoxide because with the former gas we always have "automatically" the mixture of CO and of CO_2 in the exact proportions corresponding to equilibrium with free carbon, while with the latter there is always a small excess of CO which must decompose in contact with the steel, depositing on it "carbon in excess." This makes itself felt markedly when considerable quantities of gas are used.

Fig. 60 reproduces the edge of the section of one of the cylinders thus cemented, enlarged 60 diameters, and polished and etched with alcoholic picric acid. Seven liters of carbon monoxide was used in five hours, at 1050° C.

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[1] F. Giolitti and G. Tavanti, *Ricerche sulla fabbricazione dell'acciaio cementato*, VII: Studio di un processo di cementazione fondato sull'azione specifica dell'ossido di carbonio (*Rend. della Reale Accademia delle Scienze di Torino*, 1910).

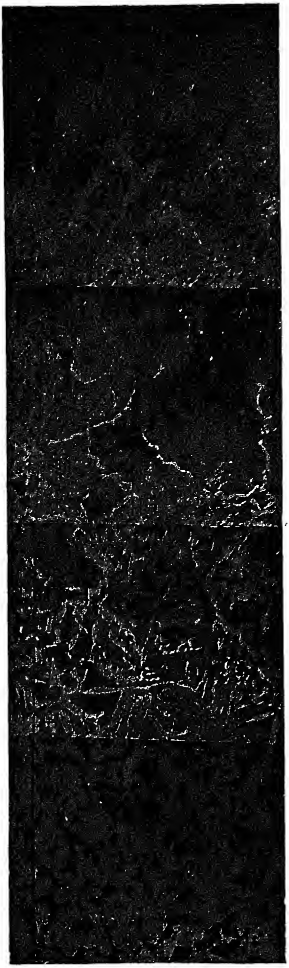

FIG. 60.

Compare this micrograph with Fig. 38, which reproduces at the same enlargement the edge of the section of a cylinder of the same steel, cemented with *ethylene* under identical conditions (at 1050° for five hours with seven liters of gas).

The comparison of the two micrographs shows at once the profound difference between the strong and sudden variations in the concentration of the carbon which present themselves in the cemented zone obtained with the use of ethylene (Fig. 38), and the continuous and gradual variation of this concentration which manifests itself in the steel cylinder cemented with carbon monoxide and carbon (Fig. 60). In fact, in the former case we first pass suddenly from the external hyper-eutectic zone (with a total thickness of 1.2 mm) to the eutectic zone (0.7 mm. thick), and from this we again pass suddenly to the hypo-eutectic zone, in which the concentration of the carbon falls from 0.9% to the value which it had in the original soft steel, within an interval of less than 0.5 mm. In the second case, on the other hand, the hyper-eutectic zone is lacking, and the purely eutectic zone (about 1.1 mm. thick) gradually connects with the hypo-eutectic zone, in which the concentration of the carbon varies continuously and gradually, through an interval of more than 2 mm., from the maximum value 0.9% (at a depth of about 1 mm.) where the first fine filaments of ferrite begin to appear, to the value which it had in the original soft steel.

These observations therefore fully

confirm the views which I have expressed, both as regards the relations which exist between the distribution of the carbon in the cemented zones before and after the slow cooling,[1] and as regards the more uniform initial—and therefore also final—distribution of the carbon that can be obtained by the use of definite cements.

This explains how, in the cemented zone obtained by the new process, under the conditions just indicated, both the causes of brittleness due to the liquation of the cementite and to the liquation of the ferrite are totally eliminated (*cf.* pp. 108 and 110).

The following table shows the results of a series of cementations carried out under the conditions named, passing 1 liter of CO_2 through the apparatus every forty minutes.

Number	Temperature (degrees C.)	Time of cementation (hours)	Thickness of hyper-eutectic zone (mm.)	Thickness of eutectic zone (mm.)	Thickness of hypo-eutectic zone (mm.)	Total thickness of cemented zone (mm.)
1	1000°	2	....	0.5	0.5	1.0
2	1000°	6	....	1.0	1.2	2.2
3	1000°	12	....	1.5	1.5	3.0
4	1000°	36	2.2	1.0	3.2	6.4
5	1060°	2	....	0.7	1.2	1.9
6	1060°	6	....	1.5	1.5	3.0
7	1100°	2	....	1.0	1.4	2.4
8	1100°	6	....	1.6	1.9	3.5
9	1100°	12	1.4	1.6	2.5	5.5
10	1200°	2	....	1.2	2.0	3.2
11	1200°	6	....	1.8	3.5	5.3

Leaving aside for the present considerations of a practical nature, which we shall consider later, it is seen at once how the data demonstrate that the specific action of carbon monoxide (as "equalizer" of the concentration of the carbon) manifests itself in cementations carried out under widely varying conditions. In the deeper cementations (Experiments 4 and 9) the action of the carbon monoxide can not be exercised completely, and a hyper-eutectic zone, relatively thin, appears. In these cases the equalization of the carbon is produced if we "isolate" for a certain time the action of the carbon monoxide, by making it act alone on the cemented steel after having removed the stronger antagonistic cement, in this case free carbon.

As proof of this I give in the following table the results obtained by reheating twice in succession, at 1000° C., in an atmosphere of pure carbon monoxide, a cylinder of soft steel first cemented in such a way as to show a marked hyper-eutectic zone:

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[1] It is clear that in the specimen shown in Fig. 60 a certain liquation of the ferrite has also taken place; this is shown by the presence in this specimen of the external zone of pure pearlite. On the other hand, the measure of the liquation varies enormously from the one specimen to the other.

	Thickness of hyper-eutectic zone (mm.)	Thickness of eutectic zone (mm.)	Thickness of hypo-eutectic zone (mm.)	Total thickness of cemented zone (mm.)	Total time of heating at 1000° in carbon monoxide (hours)
(*a*) In original cylinder.....	2.1	0.9	1.8	4.8	....
(*b*) After first heating (7 hours at 1000° C.).	....	3.7	3.2	6.9	7
(*c*) After second heating (8 hours at 1000° C.)	....	....	8.5	8.5	15

The table clearly shows the efficacy of carbon monoxide as an agent for diffusing or equalizing the carbon in the steel. Of the mechanism of this action, I have already spoken (see p. 86).

It is quite probable that an analogous process of "equalization," observed by Portevin and Berjot[1] in a specimen of cemented steel heated for a long time in a mass of cast-iron turnings, was also due to the agency of carbon monoxide formed by the action of the oxygen of the air occluded in the cast-iron turnings on the carbon of the latter. The paper of Portevin and Berjot contains interesting practical data, which I will review later.

The important part which is taken by carbon monoxide in the process of cementation is shown still better by a second series of experiments, carried out under the same conditions as the preceding ones but using, instead of the granular carbon prepared as we have described above, a fine powder of this same wood charcoal, employing only that part of the carbon which passes through a sieve of 81 mesh to the sq. cm. The results of these experiments are collected in the following table:

Number	Temperature (degrees C.)	Time of cementation (hours)	Thickness of eutectic zone (mm.)	Thickness of hypo-eutectic zone (mm.)	Total thickness of cemented zone (mm.)	Max. concentration of C in hypo-eutectic zone, %	Remarks
1	1000	2	....	1.0	1.0	0.70	Horizontal furnace.
2	1000	6	....	1.2	1.2	0.70	Horizontal furnace.
3	1000	2	....	0.6	0.6	0.60	Vertical furnace.
4	1000	6	0.5	0.4	0.9	0.90	Vertical furnace.

These data prove in a conclusive manner what I have asserted above. It is evident, in fact, that if the diffusion of the carbon into the steel were due to the direct action of the solid carbon placed in contact with it, the cementation should take place considerably more rapidly in the experiments reported in the last table than in those I carried out under identical conditions, reported in the first table; for it is clear that the contact between the steel and the carbon is considerably more intimate when the latter is used in the form of a fine powder than when it is used in granular form. In the cementation reported in the last table the velocity of penetration of the carbon is considerably lower than in the corresponding experiments of the table reproduced on p. 135; this is an evident proof of the slight *direct* action of the carbon (by contact) and of the preponderant action of carbon monoxide as "vehicle" for the penetration of the carbon into the steel. In fact, the velocity of the penetration of the carbon is greater the more freely the carbon monoxide can circulate around the carbon and the steel, with which it must react alternately, as I have before indicated. Further confirmation of this is seen by a comparison of Experiments 1 and 3 of the table above; this comparison shows, in fact, that the cementation is considerably less deep when, keeping all the other conditions equal, the porcelain tube acting as cementation chamber is arranged vertically instead of horizontally. It is evident that while the vertical arrangement favors the contact between the carbon powder and the surface of the steel cylinders, it renders the circulation of the gases in the apparatus considerably more difficult.[1]

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[1] *Revue de Métallurgie*, 1910, pp. 61–75.

These observations explain the results which are obtained in practice in cementation effected with powdered mixtures of wood charcoal and barium carbonate.

There still remained to be investigated one quite important point for the technical application of the process, *viz.*, concerning the limits of "space" in which carbon monoxide can still efficiently exercise its characteristic specific function as "vehicle" in the transportation of the carbon from the solid cementing mass to the mass of steel. The importance of defining practically these limits is evident to anyone familiar with the technique of ordinary cementation carried out with solid cements, for he knows how difficult it is to operate under such conditions as to be absolutely sure that imperfect contact of the cement with any section of the surface of the piece to be cemented will not leave dangerous gaps in the carburized zone.

For this investigation we used the following arrangement: Having arranged our furnace vertically, we placed in the center of it, and along the axis of the cementation chamber, a cylinder of the usual soft steel, 30 cm. long and 10 mm. in diameter. Along a length of the cylinder were made file marks, 1 cm. distant from each other, numbered progressively from 1 to 29, starting from the lower end of the cylinder. Only the lower part of the cylinder was immersed, for a length of 13 cm., in the usual mass of granular wood charcoal; the upper portion, on the contrary, remained entirely free.

While a slow current of carbon monoxide (about 2 liters per hour) circulated through the apparatus, entering from the bottom, we raised the temperature of the cementation chamber to 980°, keeping it constant there for four hours. Having allowed the apparatus to cool slowly, we cut the steel cylinder longitudinally along a plane passing through its axis, and on the section thus obtained, polished and etched in the usual way, we were easily able to observe under the microscope the variations in structure of the cemented zone along its whole length. I report in the table below the results of some of our observations:

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[1] This last fact is clearly observed when carrying on the experiment.

Position of observed section of zone on scale on cylinder	Thickness of eutectic zone (mm.)	Thickness of hypo-eutectic zone (mm.)	Maximum concentration of carbon in hypo-eutectic zone	Remarks
5.0	0.6	1.2	0.9%	Part immersed in the carbon.
10.0	0.6	1.1	0.9	Part immersed in the carbon.
13.0	0.6	1.1	0.9	Part immersed in the carbon.
13.5	0.6	1.1	0.9	Part not immersed in the carbon.
14.5	0.3	1.2	0.9	Part not immersed in the carbon.
16.0	....	1.5	0.65	Part not immersed in the carbon.
19.0	....	1.2	0.5	Part not immersed in the carbon.
20.0	....	1.2	0.4	Part not immersed in the carbon.
26.0	....	1.1	0.3	Part not immersed in the carbon.

The data contained in the preceding table show clearly how, in the process with which we are dealing, the cementation takes place, by the action of carbon monoxide, with full efficiency even in the sections of the surface of the steel which are not in direct contact with the granular mass of carbon but are about a centimeter distant from it, and that the efficiency of the cementation is diminished only in the parts of the surface of the steel considerably more distant (5–6 cm.) from the carbon.

We shall deal, in the second part of this volume, with the data contained in several other recent publications,[1] for they are data of essentially practical interest; as, for example, the course of the cementation of special steels for deep cementation, the best conditions for tempering cemented steels, etc.

Before closing this chapter, however, I want to report the results of some more recent investigations which, although rather of a theoretical character, nevertheless present much interest from the practical point of view.

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[1] As an example, among the publications of this period, the contents of which I consider it superfluous to cite here, I call attention to a memoir presented by Grayson before the Iron and Steel Institute (1910, Vol. I, pp. 287–302). In this memoir the author does, in truth, reproduce several "concentration-depth" diagrams; but (even leaving aside the fact that these diagrams appeared a long time after those already published by me and my collaborators), Grayson does not deduce from them any of the important conclusions which we have seen can be drawn from an accurate study of these diagrams.

Moreover, Grayson studies the effects of four solid cements, of which he indicates only the *elementary* composition but ignores their *constitution*. It is clear that under these conditions the results obtained can be only of small importance.

Referring briefly to some observations contained in a recent work of J. Kirner;[1] they are at present very incomplete, but may probably open the way for interesting researches. The author examines the behavior of two nitrogenous cements and of one free from nitrogen. For the first one, not knowing its constituents, he indicates the composition resulting from analysis; besides the carbon, it contained 41% of sodium chloride, 9% of total nitrogen, 0.5% of sulphur, and 18% of a residue insoluble in water, consisting principally of Fe_2O_3, Al_2O_3 and CaO. This cement he designates by the letter A_1. The second nitrogenous cement, which he designates C_1, consisted of leather carbon. The third, a non-nitrogenous cement (B_1), was of wood charcoal mixed with alkaline carbonates.

At 700° C. both nitrogenous cements (A_1 and C_1) furnish a thin cemented zone with less than 0.55% C but *very rich in nitrogen*, the percentage of which exceeds 0.5% in the zone obtained with the cement C_1 and 0.6% in that obtained with the cement A_1. In these cemented zones the author observes a special constituent which he designates by the name "flavite," the proportion of which increases with increase in the content of nitrogen. This constituent appears with "the aspect of a solid solution" (?) in sections of the heated steels etched with picric acid, while it disappears in these steels when hardened.

At 900° C. the cemented zones obtained with cement A_1 contain a much smaller quantity of nitrogen (0.035%) than that contained in the zones obtained under the same conditions with cement C_1 (0.15%). At 1000° C. the proportion of nitrogen absorbed by the steel becomes very small for both cements.

As to the intensity of the carburization, while in the zones obtained with the non-nitrogenous cement B_1 the mean concentration of the carbon increases gradually and continuously with rise in the temperature, in the zones obtained with the two nitrogenous cements (A_1 and C_1) the mean concentration of the carbon does not increase appreciably when the temperature of the cementation varies from 700° to 900° C., and begins to rise markedly with the temperature only when the latter goes above 950° C.

These experiments appear to show with great probability two things: the possibility that certain nitrogenous cements under definite conditions give rise to the diffusion of considerable proportions of nitrogen into the steel, and the influence exercised by nitrogen on the course of the cementation. It is to be regretted that the authors omit a description of their method for the quantitative determination of the nitrogen.

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[1] J. Kirner, *Ueber einige bemerkenswerte Beobachtungen beim Einsatzhärten von Stahl, imbesonderen hinsichtlich der Wirkung des Stickstoffs* (*Metallurgie*, 1911, Vol. VIII, pp. 72–77).

Since even small quantities of nitrogen can exercise great influence on the mechanical properties of steel, it is quite probable that a series of investigations carried out as above would lead to interesting results.

CEMENTATION OF NICKEL STEELS

Some recent investigations on the cementation of nickel and of chromium steels are worth citing. The data relative to the first—the nickel steels—are collected in two papers[1] published in the first half of 1911.

Leaving aside a detailed exposition of the data regarding the concentration and the characteristic distribution of the carbon in the cemented zones obtained by working under various conditions with steels of varying nickel content, I here summarize the more general conclusions which can be reached from these data.

The experiments were carried out by cementing successively at various temperatures ranging between 900° and 1100° C., with ethylene, with carbon monoxide and with the *mixed* cement of which I have already spoken (carbon monoxide and carbon), soft steels containing 2%, 3%, 5%, 25% and 30% of nickel, respectively.

The principal conclusions are the following:

1. The course of the cementation of steels with 2 to 3% of nickel is practically identical with that of the cementation of carbon steel equally carburized.

2. When the nickel content exceeds 3%, the maximum concentration of the carbon in the cemented zones decreases with increase in the percentage of nickel contained in the steel.

The following table contains data relative to the maximum concentrations reached by the carbon in the cemented zones when cementing, under various conditions, steels of varying nickel content.

No.	Conditions of cementation	Nickel content				
		2%	3%	5%	25%	30%
1	Carbon monoxide (16 liters) 5 hours at 950°	......	0.38	0.23	......	0.15
2	5 hours at 1050°	......	0.35	0.35	......	0.17
3	Ethylene 5 hours at 950°	1.12	......	0.93	......	0.39
4	5 hours at 1050°	......	1.53	1.28	0.84	0.63
5	Mixed cement 2 hours at 1000°	0.70	......	0.70	......	0.67
6	2 hours at 1100°	0.92	......	0.74	......	0.40
7	5 hours at 1000°	1.12	......	0.80	0.64	......
8	5 hours at 1050°	0.83	......	0.73	0.59	......
9	5 hours at 1100°	1.07	......	0.83	0.73	......

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[1] F. Giolitti and F. Carnevali, *Sulla cementazione degli acciai al nichelio*, I (*Atti della R. Accademia delle Scienze di Torino*, Vol. XLVI, February 19, 1911); and F. Giolitti and G. Tavanti, *Sulla cementazione degli acciai al nichelio*, II (*Rassegna Mineraria, Metallurgica e Chimica*, Vol. XXXIV, No. 18, June 21, 1911.)

For detailed experimental data relative to the curves of the distribution of the carbon, to the composition of the steels used, etc., and for the particular conditions of the individual experiments, I must refer the reader to the two original papers.

3. Under the same experimental conditions, the variations in the concentration of the carbon in the cemented zones are more gradual and more uniform in nickel steels than in carbon steels. This is one of the reasons which make it advantageous to use nickel steel for cemented pieces which are to be subjected to shocks and which must, therefore, show the minimum brittleness compatible with the required surface hardness. This advantage clearly results from the "exfoliation" of cemented and hardened pieces. The phenomenon just mentioned is due, at least in part, to the fact (proved by microscopical examination) that in nickel steels the phenomenon of liquation in the mixed crystals manifests itself, under equal conditions, with less intensity than in carbon steels.

4. In pearlitic nickel steels, or those belonging to the first transition zone of Guillet's diagram, the region of passage from the hyper-eutectic to the eutectic layer in the cemented zone corresponds to a carbon content (0.6–0.65%) lower than that of the corresponding zone (the eutectic zone) of cemented carbon steels (0.9%).

5. The specific action of carbon monoxide is exercised in the cementation of nickel steels in a manner entirely analogous to that in which it is exercised in the cementation of carbon steels. The use of the mixed cement with carbon monoxide as base presents, therefore, in the cementation of nickel steels the same advantages which we have already seen for the cementation of carbon steels.

6. The "velocity of cementation" (meaning the *depth* reached in a given time by the carburized zone) is, using mixed cement, slightly higher for nickel steels than for carbon steels.

CEMENTATION OF CHROME STEELS

Cementation experiments made on a chrome steel with 2.33% of chromium,[1] using successively as cements ethylene, pure carbon monoxide, and the usual mixed cement with carbon monoxide as base ($CO + C$), showed first of all that the characteristic mode of action of each of the three "typical cements" just indicated is exercised toward chrome steel just as we found it for carbon steels. In general, however (and this presents great interest in practice), it is clearly observed that the presence of the chromium tends to an increase in the maximum concentration of the carbon in the cemented zones, when we take as basis the value which this concentration reaches in carbon steels subjected to cementation under identical conditions.

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[1] F. Giolitti and F. Carnevali, *Sulla cementazione degli acciai al cromo* (*Atti della R. Accademia delle Scienze di Torino*, Vol. XLVI, April 2, 1911).

An approximate idea of the extent of this increase may be obtained from the data of the following table, in which are given the maximum concentrations of the carbon in the cemented zones obtained with the steel having 2.33% of chromium and 0.4% of carbon, working under the different conditions indicated in the table. For more precise data on the experimental conditions and on the results (especially as regards the distribution of the carbon in the cemented zones) I must refer back to the original paper.

No.	Cement used	Temperature	Length of cementation (hours)	Maximum concentration of carbon in cemented zone
1	Ethylene	950°	5	1.40%
2	Ethylene	1050°	5	1.30
3	Carbon monoxide	950°	5	0.60
4	Carbon monoxide	1050°	5	0.52
5	Mixed cement (CO + C)	1000°	2	0.81
6	Mixed cement (CO + C)	1100°	2	0.91
7	Mixed cement (CO + C)	1000°	5	1.22
8	Mixed cement (CO + C)	1100°	5	1.21

CEMENTATION UNDER PRESSURE

The course of the cementation of special steels with cements whose carburizing action is due chiefly to carbon monoxide, and of the phenomena of oxidation which often accompany it, is cleared up greatly by a series of recent investigations using the mixed cement of wood charcoal and carbon monoxide under pressures higher than atmospheric.

A part of these results was communicated at a meeting of the Iron and Steel Institute held in October, 1911.[1] We will review them here at some length.

I have already cited on page 126 a series of experiments bearing on the relation between the pressure of the carburizing gas and the depth and the intensity of the cementation obtained, when using cements whose activity is due chiefly to the specific action of carbon monoxide. These gave clear proof of the direct and preponderant function of the carburizing gases (and especially of the carbon monoxide) in the process of the cementation.

The apparatus used in the experiments which I now report is shown in perspective in Fig. 61; it was similar to that already described as being used in the experiments just cited, differing essentially only in the devices which made it more gas-tight. This is essential for the exact determination of the velocity of the current of carbon dioxide which reaches the cementation box.

The longitudinal section is reproduced in the accompanying figure (Fig. 62).

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[1] F. Giolitti and E. Carnevali, *On Case Hardening by means of Compressed Gases* (*The Journal of the Iron and Steel Institute*, 1911).

A and *B* are connectors fastened to rods which pass (electrically insulated and gas-tight) through the walls of the cast-iron vessel *C* and carry the heating current to the spiral of nickel wire *D*. This spiral is wrapped around the porcelain tube *E*, which can easily be put in position and removed from the apparatus, in which it is simply placed in a larger tube of refractory earth *F*.

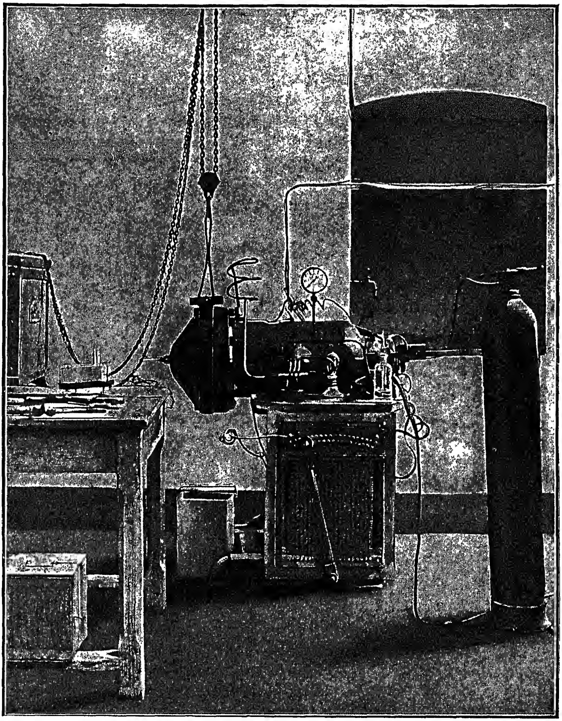

FIG. 61.

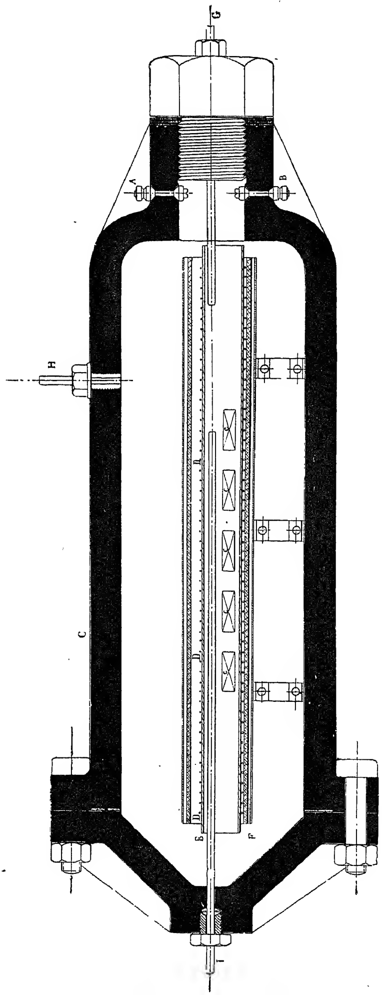

FIG. 62.

The space between the tube *F* and the wall of the cast-iron vessel is filled with asbestos. The gas (CO_2) enters through the tube *G* and issues through the tube *H*. The strong porcelain tube *I* protects the thermo-electric couple for measuring the temperature throughout the whole length of the cementation chamber; near it are placed the pieces *C* to be cemented, wholly surrounded by the granular carbon. The apparatus to regulate and indicate the pressure is seen in Fig. 61. It is identical with that which I have already described on p. 129.

The experiments were carried out similarly to those already described (see p. 130), using granular wood charcoal, carbon dioxide and cylinders of different steels of the following compositions:

1. Ordinary soft carbon steel, which I shall designate as *Steel "C"*:

Carbon	0.11 percent.
Silicon	0.05 percent.
Manganese	0.54 percent.
Sulphur	0.02 percent.
Phosphorus	0.04 percent.

2. Soft steel with 2% of nickel, which I shall designate as *Steel "Ni ^{2}"*:

Nickel	2.03 percent.
Carbon	0.10 percent.
Silicon	0.26 percent.
Manganese	0.41 percent.

3. Soft steel with 5% of nickel, which I shall designate as *Steel "Ni ^{5}"*:

Nickel	5.02 percent.
Carbon	0.118 percent.
Silicon	0.20 percent.
Manganese	0.47 percent.

4. Steel with 25% of nickel, which I shall designate as *Steel "Ni ^{25}"*:

Nickel	24.92 percent.
Carbon	0.17 percent.
Silicon	0.10 percent.
Manganese	0.28 percent.

5. Steel with 2.3% of chromium, which I shall designate as *Steel "Cr"*:

Chromium	2.33 percent.
Carbon	0.41 percent.
Silicon	0.15 percent.
Manganese	0.60 percent.

6. Chrome-nickel steel, which I shall designate as *Steel "Cr-Ni"*:

Chromium	1.50 percent.
Nickel	3.17 percent.
Carbon	0.33 percent.
Manganese	0.43 percent.
Silicon	0.06 percent.

In all these steels, the contents of sulphur and phosphorus were less than 0.04%.

Table I shows the conditions under which the individual cementations were carried out, and some pertinent observations on the state of the surface of the various steels after the cementation (see Table I below).

The variation of the concentration of the carbon in the cemented zones was determined by microscopic examination for the steels "C," "Ni^{2}" and "Cr," for which such an examination can furnish sufficiently precise indications. Table II contains the results of this examination.

TABLE I

Number	Steel used	Length of cementation (hours)	Pressure of gas (kg. per sq. cm.)	Interval of temperature within which cementation is effected	Velocity of gas (CO_2) (liters per hour per sq. dcm. of surface to be cemented)	Observations on the state of the surface of the cemented steel
I	C	3	15	900°–955° C.	1.5	Surface unchanged.
II	C	3	15	1020°–1050°	1.5	Surface unchanged.
III	C	2:30′	25	890°–960°	1.5	Thick layer of compact oxide.
IV	C	3	25	980°–1015°	3.0	Strong oxidation.
V	Ni^{2}	3	15	955°–975°	1.5	Surface unchanged.
VI	Ni^{2}	3	15	1035°–1045°	1.5	Surface unchanged.
VII	Ni^{2}	2:30′	25	905°–955°	1.5	Slight oxidation.
VIII	Ni^{2}	3	25	1030°–1050°	3.0	Surface unchanged.
IX	Ni^{5}	3	15	850°–890°	1.5	Surface unchanged.
X	Ni^{5}	3	15	945°–995°	1.5	Surface unchanged.
XI	Ni^{5}	2:30′	25	840°–930°	1.5	Thick layer of compact oxide.
XII	Ni^{5}	3	25	875°–915°	3.0	Thick layer of compact oxide.
XIII	Ni^{25}	3	15	870°–930°	1.5	Surface almost unchanged.
XIV	Ni^{25}	3	15	1000°–1045°	1.5	Surface unchanged.
XV	Ni^{25}	2:30′	25	870°–950°	1.5	Thin layer of non-compact oxide.
XVI	Ni^{25}	3	25	942°–980°	3.0	Slight oxidation.
XVII	Cr	3	15	935°–965°	1.5	Slight oxidation.
XVIII	Cr	3	15	1035°–1060°	1.5	Thick layer of compact oxide.
XIX	Cr	2:30′	25	900°–965°	1.5	Thick layer of compact oxide.
XX	Cr	3	25	1010°–1035°	3.0	Thick layer of compact oxide.
XXI	Cr-Ni	3	15	810°–850°	1.5	Strong oxidation.
XXII	Cr-Ni	3	15	875°–915°	1.5	Thick layer of compact oxide.
XXIII	Cr-Ni	3	25	810°–845°	3.0	Thick layer of compact oxide.
XXIV	Cr-Ni	2:30′	25	850°–900°	1.5	Thick layer of compact oxide.

For the three other steels—"Ni^{5}," "Ni^{25}" and "Cr-Ni"—for which the microscopic examination could not furnish definite results, gravimetric determinations were made on samples obtained by removing successively from the cemented cylinders coaxial layers about a quarter of a millimeter thick.[1]

Gravimetric carbon analyses were also made in the same manner on layers of the cylinders of the steel "Cr," for the purpose of determining with precision the importance of a strong hyper-increase in the carbon content of the first thin surface zone which the microscopic examination had revealed.

TABLE II

Number of cementation (see Table I)	Thickness of hyper-eutectic zone (mm.)	Thickness of eutectic zone (mm.)	Thickness of hypo-eutectic zone (up to about 0.4% of carbon) (mm.)
I	0.4	0.3	0.5
II	1.3	0.8	0.4
IV	0.7	0.6	0.4
V	0.25	1.1	0.35
VI	0.9	0.8	0.7
VIII	0.9	0.7	0.8
XVII	0.1	1.0	? (*a*)
XVIII	0.15	1.0	?
XX	0.8	1.7	?

(*a*) For the chrome steel of the composition of that used by us, the precise microscopic determination of the hypo-eutectic zone is quite difficult.

The results of these analyses are collected in Table III.

TABLE III

Number of cementation (see Table I)	Concentration of the carbon		
	In first layer (0.25 mm.), percent.	In third layer (depth, 0.7 mm.), percent.	In fifth layer (depth, 1 mm.), percent
IX	0.71	...	0.12
XIII	0.57	0.54	...
XXI	0.45	...	0.54
XVII	2.22	...	1.03
X	0.99	...	0.29
XIV	0.90	0.32	...
XXII	0.76	...	0.49
XVIII	3.1	...	1.39
XII	0.73	...	0.36
XVI	0.61	0.37	...
XXIII	0.54	...	1.56
XX	2.37	...	1.40

These experimental data furnish some interesting conclusions, which I summarize here briefly, limiting myself to those which are of general interest.

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[1] In order to be able to cut the successive layers of the cemented steels in Experiments IX, X, XII, XX, XXI, XXII, XXIII, it was necessary to reheat them for five hours at about 550° C. in a neutral atmosphere. It is known that heating under such conditions does not modify in any way the characters of the cemented zones.

These conclusions, although of an essentially general character, indicate the methods to be followed in any special case in order to fix with certainty practical rules for avoiding definite disadvantages and for obtaining given results. It is clear that the consideration of special cases which may arise in practice can not be undertaken here.

A first deduction from the experimental data is the effect which variations in the pressure of the carburizing gas exercise on the depth of the cementation, and on the concentration of the carbon in the cemented zones. This fact confirms fully the results of the earlier experiments,[1] extending them to the special steels of various types now in question. The correctness of this assertion is seen clearly from a simple comparison of the data just cited with each other and with those which I cited previously, on page 135, relative to cementations of carbon steels and of special steels carried out with the same mixed cement as used in the present experiments, but working under atmospheric pressure.

The greater pressure of the carburizing gas increases the concentration of the carbon in the cemented zones, and confirms the conclusions drawn previously as to the *direct* function of carbon monoxide in the cementation with the mixed cement.

A second fact results clearly from the comparison of the results of Experiment VI with those of VIII, of IX with XII, of XVIII with XX, and of XXI with XXIII. These comparisons show, in fact, how an increase in the velocity of the current of carbon dioxide tends to cause a decrease in the intensity of the cementation, thus eliminating, in the four pairs of experiments just cited, the effects of the increase in the pressure. These effects, as we have seen, manifest themselves with marked intensity when the cemented zones obtained by working under various pressures (ordinary pressure and pressures of 15–25 kg. per sq. cm.) but with currents of carbon dioxide of equal velocity are compared with each other.

In cementations carried out with cements based on the action of the carbon monoxide, true states of complete chemical equilibrium are never reached, so that the final characteristics of the cemented zones obtained depend to a very marked degree on the relations between the velocity of the individual reactions which take place in the course of the cementation.

The surface oxidation of the cemented steel is a third phenomenon which presents great interest, both from the theoretical and the practical point of view, and which the experimental data reported in the preceding pages (especially in Table I) show to occur with special frequency and intensity in cementations carried out under strong pressures with the mixed cement and carbon monoxide.

An oxidation of this kind had already been observed by Charpy in 1909,[2] in subjecting to the action of pure carbon monoxide, at 1000° C., chromium, manganese and various chrome steels (containing from 1.99% to 7.71% of chromium) and chromium-nickel steels (containing from 2.08% to 6.45% of nickel and from 0.70% to 7.04% of chromium).

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[1] See p.130 .

[2] *Revue de Métallurgie*, May, 1909, Vol. VI, pp. 505–518.

Charpy had observed that in using these special steels as filings the carbon monoxide is decomposed by the chromium and there occurs "*simultaneously the oxidation of the chromium and the carburization of the iron; the two elements behave as if they had been isolated.*" Charpy then adds that "when, instead of working with filings, pieces of considerable dimensions are used, the same phenomena are no longer observed; the oxidation of the chromium is produced only in the surface layer, and below the cementation proceeds regularly by diffusion."

Charpy concludes, on the basis of his experiments, that "the action of carbon monoxide at 1000° C., which is one of cementation for iron, as well as for tungsten and perhaps for nickel, is therefore one of oxidation for chromium and manganese, and may be represented by the equations:

$$\mathrm{Mn} + \mathrm{CO} = \mathrm{MnO} + \mathrm{C}$$
$$2\mathrm{Cr} + 3\mathrm{CO} = \mathrm{Cr_2O_3} + 3\mathrm{C}."$$

I have already pointed out[1] how these conclusions drawn by Charpy from his most interesting experiments were premature[2] and especially in the fact that they did not take into account at all the results of the important investigations on the action of carbon monoxide on the metals of the iron group which Schenck had published some time before.[3]

In fact Schenck's investigations—the results of which I have used extensively in my technical studies of the cementation of steel—had already led to referring to a single principle the oxidizing action of carbon monoxide on the various metals of the iron group, thus making it possible to greatly simplify the theoretical treatment of the reactions which take place in the systems consisting of the metals, carbon monoxide, carbon dioxide, carbon and the products of the oxidation and of the carburization of the various metals.

Our experiments, the results of which I have summarized in the preceding pages, give concrete form (though certainly not definite and anything but complete) to the general laws which govern the process of the cementation of special steels with cements whose activity is due to the specific carburizing action of carbon monoxide.

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[1] See p. 112.

[2] We shall see, in fact, in the pages that follow, how also for iron alone the action of carbon monoxide may be *simultaneously* "cementing" and "oxidizing." And so too for chromium and manganese steels, for which it is, in fact, not necessary (nor justifiable) to assume that the iron and the manganese, or the iron and the chromium, "behave as if they were isolated"; for, on the contrary, we shall see later how it is necessary to recognize that the behavior of each of these (iron and manganese, or iron and chromium) is profoundly modified by the presence of the other, with which it is *united* in the state of solid solution.

[3] *Berichte der deutschen chemischen Gesellschaft*, 1903–1907; *Zeitschrift f. Elektrochemie*, 1904.

But, before examining these experimental results from this point of view, it is necessary to recall briefly some physico-chemical laws relative to the action of carbon monoxide on metals, to show how these laws can be applied in our case.

If we consider the diagram of complete isothermal equilibrium, studied by Schenck,[1] in the case in which the metal subjected to the action of the carbon monoxide is iron alone and for the temperatures at which solid solutions (mixed crystals) of iron carbide in the iron can not be formed (that is, below 700° C.), we find five equilibrium curves corresponding to five distinct reactions. Representing, as usual, on the axis of abscissas the concentration (x) of carbon monoxide in the mixture of carbon monoxide and carbon dioxide (varying x from 0 to 1) and on the axis of ordinates the total pressures (P) of the said gaseous mixture, the five curves are those represented in the accompanying figure (Fig. 63) and designated by the numbers 1, 2, 3, 4 and 5.

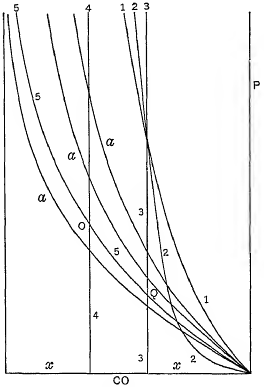

FIG. 63.

We will recall here briefly the significance and the equation of each of these curves:

Curve 1. Cubical hyperbola $\frac{x^2}{1-x}P=\mu$ ($\mu=$ constant); corresponding to the conditions of equilibrium of the system (Fe_3C, Fe, CO, CO_2).

Curve 2. $\frac{x^5}{(1-x)^4}P=\theta$ ($\theta=$ constant); corresponding to the conditions of equilibrium of the system (Fe_3C, FeO, CO, CO_2).

Curve 3. Straight line $\frac{x}{1-x}=\eta$ ($\eta=$ constant of reduction); corresponding to the conditions of equilibrium of the system (Fe, FeO, CO, CO_2).

Curve 4. Straight line $\frac{x}{1-x}=k$ ($k=$ constant); corresponding to the conditions of equilibrium of the system (Fe_3O_4, FeO, CO, CO_2).

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[1] In the French edition of his *Physical Chemistry of the Metals* (Trad. par Lallement, Paris; Dunod et Pinat, 1911), Schenck has summarized with great clearness the results of his most recent investigations on the problem with which we are dealing.

Curve 5. $\frac{x^2}{1-x}P = \zeta$ (ζ = constant); corresponding to the conditions of equilibrium of the system (C, CO, CO_2).

If, instead,we work at a temperature higher than 700° C., the iron carbide will be able to form solid solutions with the iron, and there must appear in the equilibrium diagram, besides the five curves already indicated, the equilibrium curves of the systems resulting from the addition to the preceding constituents of iron-carbon mixed crystals.

To every value of the concentration of the carbon in the mixed crystals, there corresponds an equilibrium curve whose equation (in the case in which the mixed crystals are present in sufficient amount so that their concentration does not vary sensibly with variation—within certain limits—of the pressure of the gaseous mixture) is also that of a cubical hyperbola of the form $\frac{x^2}{1-x}P = \nu$; analogous, therefore, to that of the systems (Fe, Fe_3C, CO, CO_2) and (C, CO, CO_2). Among all these cubical hyperbolas, constituting a pencil and all passing through the point ($x = 1$, $P = O$),[1] one presents special interest for our case, in which—the cementation being effected with the "mixed cement"—the reactions take place in the presence of a large excess of free carbon ("granular" wood charcoal); this curve is that corresponding to the particular concentration of the carbon in the mixed crystals for which the constant ν has (for the same temperature) the same value as the constant ζ of the equilibrium equation of the system C, CO, CO_2. It is clear, from what we have said, that such a curve coincides throughout its whole length with the isothermal of equilibrium of the system C, CO, CO_2.

If we suppose that all the operations are carried out with sufficient slowness to always attain states of complete equilibrium which we know never really occurs exactly in practice, but which we can assume with sufficient qualitative approximation), the final concentration of the carbon in the mixed crystals will always be that corresponding to a definite value of the constant ν, equal to that which, at the same temperature, is assumed by the constant ζ of the equation $2CO \rightleftarrows CO_2 + C$. We will designate by Σ the mixed crystals in which the carbon has this particular concentration.

We can therefore infer that in the qualitative study of the reactions which are effected in the cementation with mixed cement, and which are based on the simultaneous action of the carbon and the mixture of carbon dioxide and carbon monoxide in equilibrium with it, we can separate the equilibrium curves into curves corresponding to the various concentrations of the carbon in the mixed crystals, and then consider a single one of these.

In other words, in the case of the cementation carried out with "mixed cement," the problem is reduced to the same simplicity which it has (as Schenck has shown) when the study of it is limited to temperatures below

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[1] Some of these curves are traced in the figure and indicated by the letters a, a, . . .

700° C., at which a true cementation does not take place because iron-iron carbide mixed crystals can not be formed. We can, therefore, in a first approximate examination of the course of the phenomena in the experiments cited above, limit ourselves to a consideration of the diagram consisting of the first five curves.

Since in the experiments which I have cited we always started with gaseous systems rich in carbon dioxide, working in the presence of wood charcoal (to which form of carbon Curve 5 of our diagram is meant to refer), therefore, in the case in which variations in temperature do not take place and the formation of metastable states is assumed to be excluded, the only regions of the diagram which we must take into account would be those situated to the left and below Curve 5. We will begin by examining this case.

From the diagram we see clearly how the course of the process varies radically with variation in the pressure, and in the following way:

(*a*) At pressures above those corresponding to the point O[1] (intersection of the Curves 4 and 5) there are formed simultaneously ferro-ferric oxide and mixed crystals Σ, in the presence of the wood charcoal.

(*b*) At pressures between that corresponding to this point O and that corresponding to the point Q (intersection of the Curves 3 and 5) there are formed simultaneously ferrous oxide and mixed crystals Σ, still in the presence of the wood charcoal.

(*c*) At pressures lower than that corresponding to the point Q, there are formed only mixed crystals Σ, still in the presence of the wood charcoal.

It is therefore only for pressures lower than that corresponding to the point Q that the process of cementation with the "mixed cement" can take place alone, without being accompanied by the oxidation of the metal. On this basis it must be foreseen that, by sufficiently raising the pressure of the gas in the cementation with the mixed cement, there must be obtained, even with pure iron or ordinary carbon steel, phenomena analogous to those observed by Charpy for chrome steels.

This is fully confirmed by Experiments I, II, III and IV (Table I). For the first two of these the pressure (15 kg. per sq. cm.) is lower than the pressure corresponding to the equilibrium point Q (for the temperature at which the cementation is carried out); while for the other two the pressure (25 kg. per sq. cm.) has a value higher than that which the ordinate of Q assumes at the temperature chosen for the experiment (900°–1000° C.).

In the first two experiments, therefore, the process of cementation alone takes place; while in the other two the process of cementation (formation of mixed crystals Σ) is accompanied by a strong surface oxidation of the metal.

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[1] It must be remembered that in the experiments cited here the pressure is kept constant during the whole operation by the entrance of fresh gas into the apparatus. For, if the quantity of gas were limited, it is well known that the initial minimum pressure of the carbon dioxide at which the ferro-ferric oxide is formed would be lower than the pressure corresponding to the point O.

The state of the cemented and oxidized steel cylinders merits closer examination. The cylinder cemented in Experiment 3 is covered with a compact layer of oxide about 0.7 mm. thick, in which have remained solidly fixed the pieces of granular carbon which were in contact with the surface of the metal. The metal lying beneath the oxide is intensely carburized.

This combination of facts, which on first superficial examination might appear bizarre and contradictory but which, on the contrary, are explained perfectly by the principles which I have developed, is illustrated by the three accompanying photographs (see Figs. 64, 65, and 66).

Fig. 64.

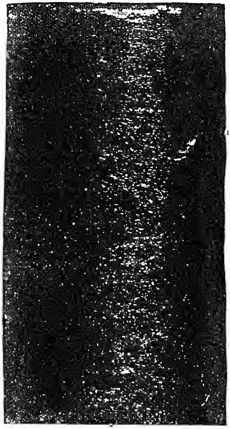

Fig. 65.

The first two photographs reproduce (enlargement 4 and 4.5 diameters, respectively) the external appearance of two regions of the cemented and oxidized cylinder; in the first are seen the fragments of carbon fixed in the iron oxide; in the second the thickness of the layer of oxide appears clearly, in the zone in which it has been broken so that the part removed has left exposed the metal lying beneath.

The third photograph reproduces (enlargement 65 diameters) a section normal to the axis of the cylinder of the steel lying directly below the layer of oxide; the appearance of this section (polished and etched with a 5% alcoholic solution of picric acid) shows that the steel is cemented and that the concentration of the carbon reaches, near the external surface of the cemented zone, about 0.85%.

The examination of the material composing the external zone, easily detachable from the cylinder, showed that it was ferro-ferric oxide (Fe_3O_4) mixed with a small quantity of carbon.[1]

The position of the two invariable equilibrium points *O* and *Q*, the significance of which we have just seen, varies with variation in the temperature and in the composition of the steel subjected to the cementation. Let us examine briefly the course of these variations.[2]

As regards the variations in the two equilibrium pressures due to variation in the temperature, let us note that the three curves 3, 4 and 5 of Fig. 63 are all displaced toward the right when the temperature rises, so that the variations in the ordinates of the points *O* and *Q* depend on the relations between these displacements. These relations vary with the composition of the steel, but in general they are such that the ordinates of the points *O* and *Q* (minimum pressures for each of the two degrees of oxidation) increase when the temperature rises.

It follows from this that the higher the temperature of cementation the higher the pressure above which the oxidation which accompanies the process of cementation begins to manifest itself, in its two degrees. In other words, the higher the temperature the wider is the range in pressures within which the cementation can be carried out with the certainty that the oxidation of the metal will not be produced.

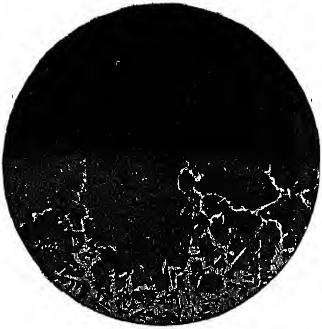

FIG. 66.

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[1] While it is easy to separate the iron oxide from the larger pieces of wood charcoal, it is not possible to separate it completely from the pulverulent carbon which is always mixed with it.

[2] From the practical point of view, the only one of these two points which presents interest is the lower one (*Q*), because this corresponds to the minimum pressure at which the oxidation of the metal to *ferrous oxide* (FeO) begins to manifest itself. The second point (*O*) corresponds simply to a change of the "*degree of oxidation*" of the metal, in the sense that at pressures higher than that corresponding to it the stable oxide is no longer the ferrous oxide FeO but the ferro-ferric oxide Fe_3O_4. It seems now, from the practical point of view, that this change is not of much importance.

A comparison of the results of the experiments already cited, taken two by two from those carried out with the same steels, confirms this assertion.[1]

The same fact is shown very clearly by the following experiment:

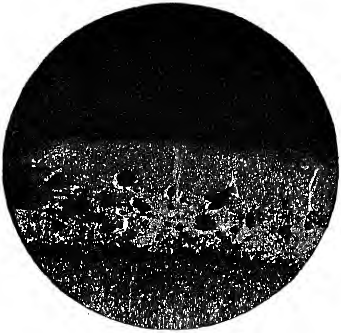

FIG. 67.

A cylinder of ordinary soft steel 60 cm. long and 1 cm. in diameter was subjected to cementation for about three hours in the usual apparatus and with the usual mixed cement, under a pressure of 15 kg. per sq. cm., care being taken to surround it completely, along its whole length, with granular carbon. The temperature, kept constant between 980° and 1035° C. for a zone of about 20 cm. near the central part of the cylinder, decreases gradually (owing to the way in which the apparatus which I have described is constructed) toward its ends until it reaches at the ends about 500° C.

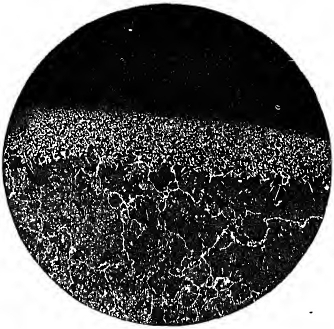

FIG. 68.

The surface of the cylinder thus treated, which is distinctly cemented throughout all the portion in which the temperature has exceeded 800° C., is perfectly unchanged in the central, hottest part (which is also the most intensely cemented), while it is covered, in the parts heated to a lower temperature, with the characteristic layer of compact oxide, in which are fixed the fragments of carbon. Beneath the layer of oxide the steel is still cemented in all parts in which the temperature has exceeded 750–800° C.

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[1] Thus, for example, compare the results of Experiments VII and VIII, and note that in the latter the velocity of the gaseous current is double that in the former.

The two equilibrium pressures vary also, as I have already said, with variation in the composition of the steel subjected to the cementation. Since in this case the curve 5 undergoes no displacement whatever, because it must always correspond to the conditions of equilibrium of the gaseous mixture with the wood charcoal, the displacements of the points *O* and *Q* will be determined exclusively by the displacements of the two straight lines 3 and 4 of Fig. 63.

Now, it is known that these two straight lines are displaced farther toward the left the more chemically inactive the metal subjected to the action of the gaseous mixture. And, since the displacement of the lines 3 and 4 carries with it the raising of the points *O* and *Q*, it follows that the more inactive the metal used the wider is the range of pressures (lower than that corresponding to the point *Q*) within which the cementation can be carried out with the certainty of not producing oxidation of the metal.

Among the metals which frequently form alloys with iron, forming mixed crystals with it, are manganese, chromium and nickel. The first two are more active metals than iron, so that with increase in their concentration in special steels, the temperature remaining constant, the two pressures *O* and *Q*, above which the cementation is necessarily accompanied successively by the two degrees of oxidation of the metal, gradually become lower. For chromium steels a relatively low chromium content (about 2–3%) is sufficient for these pressures to become (for not too high temperatures) less than ordinary atmospheric pressure. This explains the results of the investigations of Charpy (*loc. cit.*), showing them not to be due to the fact that the gaseous mixture of carbon dioxide and of carbon monoxide acts "separately on the iron and on the chromium."

Nickel, alloyed with steel, has an effect opposite to that of chromium and manganese, imparting to the solid solution with the iron, of which it forms a part, the characters of a metal less active than pure iron, so that the higher the nickel content of the steel subjected to the cementation the higher are the pressures which can be reached with the "mixed cement" without the oxidation of the metal manifesting itself.

All these deductions are fully confirmed by the results of the experiments reported in Table I.[1]

For the special steels, therefore, the phenomena with which we are dealing show effects analogous to those which I have described for the ordinary carbon steels. Thus, for example, the micrograph reproduced in Fig. 67 represents (with an enlargement of 185 diameters) a portion of the external edge of a plane section normal to the axis of the cylinder of the steel "Cr-Ni" cemented in Experiment XXIV.[2] Here, too, the cemented metal is covered with a layer of oxide in which are fixed particles of carbon.

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[1] Compare, for example, Experiment VI with XVIII, XI with XV, XVI with XXIV, etc.

[2] Etched with a 5% alcoholic solution of picric acid.

Figs. 68 and 69 (made under the same conditions as the preceding, with an enlargement of 65 diameters, after having removed the layer of oxide adhering to the cylinder) show the intense cementation which the chrome steels of Experiments XVIII and XX have undergone, although at the same time, as already observed in Table I, they have been strongly oxidized.

The same facts are observed in the nickel steels when working under pressures sufficiently high to produce the oxidation of the metal. This is clearly shown by the micrograph, Fig. 70 (Experiment VII), made under the usual conditions, enlargement of 65 diameters.

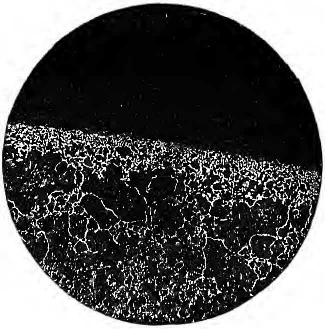

FIG. 69.

It is therefore evident that the course of the cementation of the special steels with the "mixed cement" having carbon monoxide as base is subject to the same rules which govern this process for the carbon steels. The differences for the various steels are, as we have seen, only "*quantitative*," both as regards the pressures of oxidation and as regards the concentrations of the carbon in the mixed crystals in equilibrium (along the curve 5) with the gaseous mixture (CO + CO_2), which, in its turn, is in equilibrium with the wood charcoal.

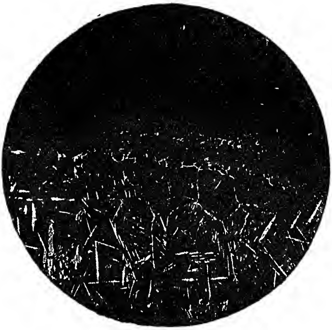

FIG. 70.

All the principles thus developed are valid as long as phenomena of metastable equilibrium do not manifest themselves, and on condition that the temperature remains constant during each cementation.

Now, both conditions are very difficult to realize experimentally, and it can be said that they are almost never realized in industrial practice. This leads to the possibility that in one or more of the phases of the cementation the point representing the system in which the reactions are effected may fall in a field of the diagram in which stable equilibrium has not been reached. Thus, for example, as the result of a lowering of the temperature, the said representative point may fall in the field situated to the right of or above the curve 5 (see the diagram of Fig. 63). In this case reactions other than those which we have thus far considered may take place; for example, the decomposition of the carbon monoxide, accompanied by the separation of free pulverulent carbon.[1] Moreover, the representative point may meet one of the two curves 1 and 2, which in their turn undergo wide displacements as the result of the variations in the temperature. In this last case the reactions which may take place are much more complex.

Before leaving this subject I wish to remark that many useful practical rules for the cementation of special steels with the mixed cement may be drawn from the information just given.

Thus, the cementation of steels of a rather high chromium content, over 4 or 5%, with the mixed cement at temperatures not higher than 1000° C., is accompanied by a marked oxidation of the metal, even when working under ordinary atmospheric pressure. But, the considerations developed in the preceding pages suggest immediately means of avoiding this oxidation; it suffices, in fact, to reduce the pressure of the gaseous carburizing mixture ($CO + CO_2$) below the minimum pressure of oxidation, Q, peculiar to the alloy at the temperature used. This can be obtained in many cases by simply diluting with air the carbon dioxide which circulates through the mass of the granular carbon. In this way the gaseous carburizing mixture acts under a partial reduced pressure, because it is "diluted" with the nitrogen of the air. Experiment confirms fully the efficacy of this method.

Finally, I shall close this chapter by citing some experimental data not referring to methods usually employed in the *normal* practice of industrial cementation, but which serve to clear up facts which sometimes present themselves accidentally in such practice, and which may occasionally also find useful technical application. The first series of these data[2] comprises the phenomena of abnormal increase in the concentration of the carbon in the cemented zones due to the formation of free cementite. I will shortly show that the occurrence of these phenomena, where under ordinary conditions the formation of free cementite can not take place, is due to the oscillations of temperature of cementation.

Exact knowledge of the relation between formation of free cementite and variation of temperature during the cementation, while it indicates the cause of the abnormal increases sometimes found in the concentration of the carbon in the cemented zones, also furnishes a means for carrying out the heating during the cementation in such a way as to purposely cause, with certainty, the formation of free cementite when it is desired to obtain cemented zones capable of taking an exceedingly high degree of hardness by quenching without its being necessary that their brittleness be reduced to a minimum.

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[1] The appearance of this new form of free carbon produces in its turn a displacement of the curve 5.

[2] See F. Giolitti and G. Scavi, *Sulla formazione della cementite* (*La Metallurgia Italiana*, September, 1911).

The phenomenon of the formation of free cementite in the processes of the direct carburization of iron in the solid state constituted for a long time one of the most important arguments[1] cited against the hypothesis of the metastability of cementite, but more recently[2] it has been recognized, on the contrary, to constitute an argument rather in favor of than against this hypothesis. An explanation had already been proposed, by Osmond[3] and Charpy,[4] and more recently and in more complete manner by Benedicks, which attributed the formation of free cementite to the oscillations in the temperature which inevitably manifest themselves during industrial cementation. Their conclusions were not founded on any *direct* experimental datum; more recent experimental studies, to which I shall now refer, have confirmed the fundamental fact assumed by those experimenters, but have shown that the "mechanism" of the phenomenon is markedly different from that imagined by them.

We have already seen how a series of cementations, carried out with cements whose activity is due to the specific action of carbon monoxide, have established with certainty the maximum values which the concentration of the carbon can reach when working under definite conditions at a constant temperature. It is clear how this result, never before attained, constitutes a sure point of departure for verifying experimentally the theory of the formation of the cementite just enunciated. It suffices, in fact, to establish a combination of conditions such that, carrying out the cementation at any *constant* temperature within a definite range, it would be quite certain (on the basis of the experimental and theoretical principles to which I have just referred) that the maximum concentration of the carbon in the cemented zones thus obtained could not exceed a given value, and especially that free primary cementite could not be formed. Given this, it is sufficient to carry out a cementation under conditions identical with the preceding but at *variable* temperatures, oscillating within *the above definite interval*, and thus find out whether in this last case the maximum concentration of the carbon in the cemented zone reaches values higher than those obtained in the preceding cementations at constant temperature, and whether free cementite is formed in this zone. If this last case is verified, it is clear that the formation of the cementite is due only to the oscillations of the temperature, and the hypothesis supported successively by Osmond, Charpy and Benedicks would have to be considered as confirmed experimentally.

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[1] See, for example, Bakhuis Roozeboom, *Journ. of the Iron and Steel Institute*, 1904, I, p. 257.

[2] See especially Carl Benedicks, *Ueber das Gleichgewicht und die Erstarrungsstrukturen des Systems Eisen-Kohlenstoff* (*Metallurgie*, Vol. 3, 1906, Nos. 12–14).

[3] *The Journal of the Iron and Steel Institute*, 1897, II, p. 143.

[4] *Comptes Rendus de l'Académie des Sciences*, 1903, 1st sem., Vol. CXXXVI, p. 1000.

The hypothetical explanation proposed by Benedicks to represent the details of the "mechanism" of the phenomenon with which we are dealing would also then be considered as probably correct.

This was proved by the experiments now to be reported:

The cementations were carried out with the usual apparatus already described in detail in the preceding pages,[1] using as carburizing substance pure carbon monoxide (supplied continuously at 1 liter per hour per square decimeter of the surface of the steel subjected to cementation) in the presence of a "granular" mass of wood charcoal, freed from ashes by washing with hydrochloric acid and placed in contact with the surface of the steel.

The cementation material was soft steel of the following composition:

Carbon	0.12 percent.
Manganese	0.36 percent.
Silicon	0.03 percent.
Sulphur	0.01 percent.
Phosphorus	0.016 percent.

Numerous experiments reported in the preceding pages show with entire certainty that when carrying out the cementation under the conditions just indicated the maximum concentration of the carbon in the cemented zones never exceeds 0.9%, and that not the smallest trace of free primary cementite is formed in these zones when working for a period not longer than six hours at any temperature between 900° and 1100° C. which is *kept constant during the whole cementation.*

Assuming this, we will now give the results of cementations carried out[2] under the conditions indicated above but *making the temperature oscillate* within the limits just indicated. In order to define in the best way the course of the thermal treatment for every experiment without digressing into minute descriptions, I give for every operation a heating diagram with abscissas proportional to the time (length of heating) and ordinates proportional to the corresponding temperatures.

These various diagrams are collected in Fig. 71.

I. Cementation of three hours at temperatures oscillating between 900° and 1000°, as indicated in Diagram I.

In the cemented zone examined under the microscope appear no traces of primary cementite, but only a eutectic zone 0.45 mm. thick and a hypo-eutectic zone in which the concentration of the carbon falls to 0.2% in an interval of 0.25 mm.

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[1] See p. 115.

[2] See F. Giolitti and G. Scavia, *Sulla formazione della cementite* (*La Metallurgia Italiana*, September, 1911).

II. Cementation of three hours at temperatures oscillating between 1000° and 1100° C., as indicated in Diagram II.

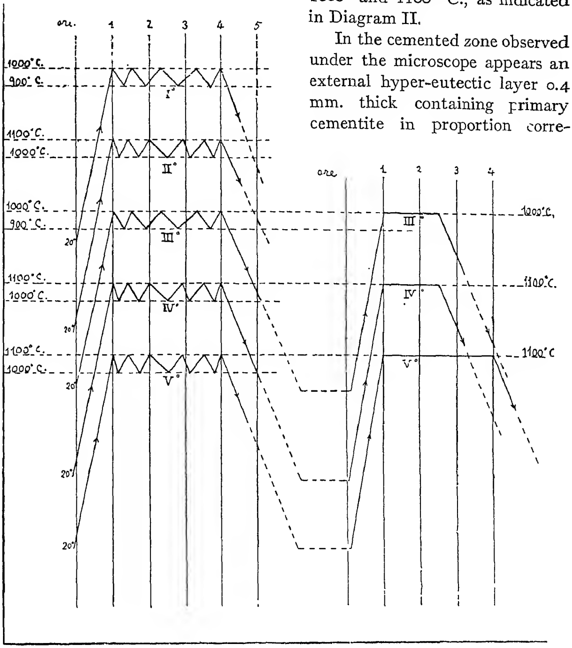

FIG. 71.

In the cemented zone observed under the microscope appears an external hyper-eutectic layer 0.4 mm. thick containing primary cementite in proportion corresponding to about 1.1% of carbon, a value confirmed by a gravimetric analysis. This layer is followed by a eutectic layer about 0.7 mm. thick, and finally by a hypo-eutectic layer in which the concentration of the carbon falls to 0.3% in an interval of about 0.65 mm.

III. One of the steel cylinders cemented in Experiment I (free from primary cementite), allowed to cool completely to the ordinary temperature, is again subjected to cementation for one hour and a half at 1000° C., *keeping the temperature constant.* Diagram III shows the total course of this thermal treatment.

In the cemented zone thus obtained, examined under the microscope, no traces of primary cementite appear. The zone is formed of an external eutectic layer 0.5 mm. thick, followed by a hypo-eutectic layer in which the concentration of the carbon falls to 0.2% in an interval of 0.7 mm.

IV. One of the steel cylinders cemented in Experiment II (with a hyper-eutectic layer of 0.4 mm. with 1.1% of carbon), allowed to cool completely to the ordinary temperature, is again subjected to cementation for an hour and a half at 1100°, *keeping the temperature constant.* Diagram IV shows the total course of this thermal treatment.

In the cemented zone thus obtained, examined under the microscope, appears an external hyper-eutectic layer 0.95 mm. thick containing primary cementite in a proportion corresponding to about 1.5% of carbon in the surface region. A gravimetric analysis of the material constituting the layer comprised between depths of 0.2 and 0.3 mm. gave the value 1.46% for the carbon content.

The hyper-eutectic layer is followed by a eutectic layer 0.4 mm. thick, followed in its turn by a hypo-eutectic layer in which the concentration of the carbon falls to 0.3% in an interval of about 0.60 mm.

V. One of the steel cylinders cemented in Experiment II (with a hyper-eutectic layer of 0.4 mm. with 1.1% of carbon), allowed to cool completely to the ordinary temperature, is again subjected to cementation for three hours at the *constant* temperature of 1100° C. in the usual mass of granular wood charcoal through which passes *a slow current of air* (about 2 liters an hour per sq. dcm. of surface of the steel subjected to the cementation). Diagram V indicates the total course of this thermal treatment.

In the cemented zone obtained in this experiment the microscope reveals an external hyper-eutectic layer about 2 mm. thick, containing primary cementite in a proportion corresponding to about 1.4% of carbon in the surface region.

From the experiments which I have now described, it is first of all evident that these results confirm fully the hypotheses of Osmond, Charpy and Benedicks, concerning the effect which oscillations in the temperature of cementation exercise in the formation of primary cementite.

The exactness of this assertion is seen from the results of Experiments II, IV and V. In these, in fact, is shown abundant formation of primary cementite, under conditions where the earlier investigations[1] have excluded the possibility of such formation taking place when carried out at constant temperature.

We can, however, see that an accurate examination of the results of these

[1] See p. 135.

experiments leads to modifying and completing in various parts the hypotheses of Osmond, Charpy and Benedicks. We will, therefore, subject these results to still further discussion.

First, a comparison of the results of Experiments III, IV and V at once shows the effect which the presence of pre-existing quantities of primary cementite, formed during a period of cooling, exercises on the further formation of cementite. In this effect there is certainly to be seen the phenomenon of the difference between the velocity of the solution of cementite in γ-iron and the velocity with which carbon passes into solution in iron by cementation. This is exactly the phenomenon to which Benedicks attributed in greater part the large increase in the concentration of the carbon and the abundant formation of cementite at oscillating temperatures.

In Experiment III, in which the cemented zone obtained in the first phase of the operation does not contain the hyper-eutectic layer, all the iron carbide liberated as the result of the cooling preceding the second phase is in the secondary state (lamellæ of pearlite); that is, in the form best adapted to making it rapidly soluble in the iron as soon as this reaches, as the result of the succeeding heating, the "γ" state. In this case, therefore, the phenomenon indicated by Benedicks (to which we have just referred) can not be produced. This our Experiment III most clearly confirms, for in its second phase (cementation of one hour and thirty minutes at 1000° C.) the concentration of the carbon has not increased in the least.

This confirmation is still clearer when we take into account the results of Experiments IV and V, in which the cementation is carried out similarly to that of Experiment III, but in such a way that by cooling between its two phases there is formed in the cemented zone a certain quantity of primary cementite, which is more slowly soluble in the γ-iron formed during the second period of heating than is the secondary cementite.

Now, in this case there is manifested in the second period a large increase in the concentration of the carbon of the cemented zone, even when in the second phase the cementation is effected under conditions which, in normal "continuous" procedure, would furnish cemented zones of a carbon concentration *lower* than that reached in the first phase. This is especially evident in Experiment V, in which the second period of the operation is carried out under conditions in which other experiments[1] have shown "continuous" cementation to furnish carburized zones containing a maximum of about 0.7–0.8% of carbon. These phenomena are explained clearly by the hypothesis of Benedicks.

But, on the contrary, this same hypothesis no longer suffices to explain the differences between the results furnished by Experiments I and II as regards the concentration of the carbon and the formation of the primary cementite in the cemented zones.

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[1] See the note already cited, and especially F. Giolitti and G. Scavia, *Sull'impiego dei forni a muffole orizzontali per la cementazione dell'acciaio con cementi misti* (*La Metallurgia Italiana*, August, 1911, pp. 332–348). See also the second part of the present volume.

In the first place, we can exclude *a priori* the supposition that the increase in the concentration of the carbon in the cemented zone obtained in Experiment II, up to the formation of a hyper-eutectic layer in the cooled specimen, can be due to a process analogous to that indicated by Benedicks—for the minimum of the oscillating temperatures is quite distant from the maximum temperature at which primary cementite separates in a carbon steel with 1.1% of carbon.

In the second place, if the cause of the formation of the cementite were exclusively that indicated by Benedicks, this same formation should manifest itself with greater intensity in Experiment I, in which the minimum of the oscillating temperature of cementation is considerably nearer than that of the following experiment to the maximum temperature at which primary cementite can begin to separate.

A plausible explanation of the phenomenon to which I have just referred, and, in general, of the increase which the oscillating temperatures exercise on the carbon of the cemented zones (even when the minimum temperature reached in these oscillations is kept distant from the maximum values at which the separation of the primary cementite from its solid solution in γ-iron can be manifested) is furnished by an accurate consideration of the equilibrium of the systems constituted by iron, carbon, cementite, the mixed iron-carbon crystals, carbon monoxide, carbon dioxide, and the oxides of iron.

The equilibrium isotherms of the various systems formed of the components mentioned above, in groupings corresponding to the reactions which can take place, have been studied recently with great care by Schenck, mostly on the basis of the experimental investigations carried out by himself and his students.

It would lead too far to review here in detail the conclusions of Schenck; I shall assume, therefore, that his results are known.[1]

Among all the cubical hyperbolas (a_1, a_2, etc., see Fig. 72) of the form

$$\frac{x^2}{1-x} P = K$$

(in which, as is well known, x represents the concentration of the carbon monoxide in the gaseous phase, P the total pressure of this gaseous phase, and K an equilibrium constant) which, for a definite and constant temperature, represent, for various values of K, the conditions of equilibrium of the gaseous phase with mixed crystals of various concentrations, one presents to us a special interest. When the operation is carried out in the presence of a large excess of wood charcoal, the constant K has the same value that the equilibrium constant of the system CO_2, CO, C (wood charcoal) assumes at the same temperature.

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[1] Rudolf Schenck, *Chimie physique des métaux.* Translated by M. Lallement, Paris, Dunod and Pinat, 1911.

This curve (which coincides throughout its whole length with the corresponding equilibrium isotherm of the system *wood charcoal*, CO, CO_2) *fixes*, in fact, the maximum concentration which the carbon can reach in the cemented zone when the cementation is carried out in the way we have indicated at a definite temperature *kept constant during the whole operation.*

Now, it is known that any variation in the temperature produces a displacement of all these curves a_1, a_2, etc. (Fig. 72). An increase in the temperature produces a displacement of these curves toward the right, while a decrease displaces the curves toward the left. It is clear that any relative retardation in the variations of concentrations of the mixed crystals and gaseous phase gives rise to states of *false equilibrium*, protracted for a more or less extended period of time according to the amount of retardation and the duration of the variations in the temperature. When, then, many opposite variations in the temperature alternate with each other, the final state of the system can be independent of these states of false equilibrium only when the retardations occur to an identical extent in two opposite directions. When this identity is absent, these retardations, caused by the oscillations in temperature, will markedly influence the final state of the system.

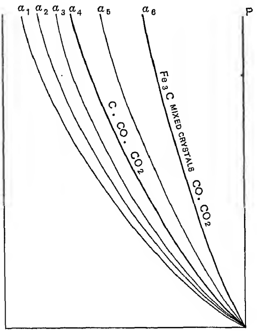

FIG. 72.

The phenomenon is in this latter case perfectly analogous to that considered by Benedicks in the separation of the cementite from the saturated mixed crystals.

To fix our ideas: as the result of a lowering in the temperature, the pencil of curves a_1, a_2, etc., is displaced toward the left, so that the point representing the composition of the gaseous phase will fall for a certain time (the length of which depends on the retardation in the establishment of equilibrium between the gaseous phase and the mixed crystals, by the separation of free carbon from the gaseous mixture) on one of the curves a_1, a_2, etc., corresponding to a carbon concentration greater than that of the curve a_4, on which it first lay.[1] It is possible that for a certain brief time this point may reach and pass the last curve to the right of the pencil, corresponding to equilibrium with free cementite. If, now, in the succeeding rise in the temperature, during which the representative point of the system will fall temporarily on one of the curves a_1, a_2, etc. (corresponding to a concentration of the carbon of the mixed crystals lower than the initial concentration a_4), the retardation in reaching complete equilibrium with the free carbon (wood charcoal) is less than that manifested in the preceding phase, the local increase in the concentration of the carbon (and the final formation of cementite) occurring in the preceding period will not be compensated. The effect of the oscillation in temperature will therefore be an increase in the concentration of the carbon above the value corresponding to the conditions of equilibrium which would have been realized if the temperature had remained constant.[1] It is also clear that these effects of the successive oscillations in the temperature may be cumulative.

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[1] The variations in the temperature produce displacements of the equilibrium curve of the system C, CO, CO_2 concordant with those of the curves of equilibrium of the gaseous

In fact, the mechanism of the phenomena which we have just set forth is identical to that proposed by Benedicks, except that our study of the phenomena of equilibrium between the gaseous phase, the mixed crystals, and the cementite explains the increases in the concentration of the carbon in the cemented zones produced by the oscillations in temperature. Even in the cases in which it is not possible to admit that the separation of the primary cementite, due to the saturation of the mass of the mixed crystals, can be produced by a simple lowering of the temperature below the point Ar_1 corresponding to the normal concentration of carbon for a cementation carried out under these definite conditions, the explanation still holds.

The effect of a definite series of oscillations in the cementation temperature on the concentration of the carbon in the cemented zone depends on such a large number of factors, so uncertain and imperfectly unkown, as to make predictions in this field practically impossible. Among these factors are: the velocity of the dissociation of carbon monoxide mixed with carbon dioxide, while lowering the temperature; the velocity of the diffusion of the gases into the iron at the various temperatures; the velocity of the reaction of the carbon of the mixed crystals upon the mixtures of carbon dioxide and carbon monoxide at the various concentrations and at the various temperatures, etc. The differences between these factors easily explain the differing results of Experiments I and II.

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phase with the iron-carbon mixed crystals. The experiments which I have cited in the preceding pages seem to show that at the various temperatures comprised between 850° and 1200° C. the first curve practically coincides with the curve of equilibrium of the gaseous phase with mixed crystals with 0.9% of carbon. This is under such conditions of approximately complete equilibrium as can be realized in the practice of cementation.

[1] I recall here that the mixed crystals whose concentrations correspond to curves of the pencil of hyperbolas lying to the *right* of the curve a_4 (see Fig. 72) are those for which further cementation can not be effected directly by the action of the carbon, but *only* by means of carbon monoxide.

The experimental data just reported and the principles which I have developed may find useful practical applications where it is desired to obtain free cementite along with an increase in the carbon content of the cemented zones above that normally obtained with a given cement, and this without modifying the chemical nature of the cement used.

It follows that the thermal treatment suitable for obtaining this result consists in an interruption of the cementation, accompanied by quick cooling of the piece being subjected to carburization.

This operation is difficult, and not practicable where the cementation is effected with solid cements in ordinary cementation boxes. It becomes easy, however, when the cementation is carried out with gaseous or mixed cements, working in apparatus specially adapted for their use.

The second group of experimental data are of an essentially theoretical interest, directly confirming the correctness of the principles set forth in the preceding pages concerning the mechanism of the carburizing action of carbon monoxide, alone or in the presence of other carburizing substances. These same data may some day find useful practical applications.

A detailed account of the experimental facts in question may be found in a paper published in *Rassegna Mineraria, Metallurgica e Chimica*, 1910, Vol. XXXIII, under the title "*Sulla fabbricazione della ghisa malleabile,*" Paper III. By F. Giolitti, F. Carnevali and G. Tavanti. These facts may be briefly summarized as follows:

If the cementation of an ordinary soft carbon steel is effected with a mixed solid-gaseous cement, in which the solid constituent is composed (instead of the usual wood charcoal) of turnings of a carbon steel of definite carbon content, and the carburizing gas consists of the usual mixture of carbon monoxide with small quantities of carbon dioxide, it is observed that the maximum concentration of the carbon in the cemented zones remains equal to the carbon in the steel turnings used, instead of reaching the 0.9% which is obtained normally with granular wood charcoal as the solid constituent of the cement.

These observations confirm the theory which I have developed, according to which the carbon monoxide (and its mixtures with carbon dioxide which are formed as the result of its carburizing action) intervenes in the cementation, when the mixed cements are used, essentially by acting as a vehicle, transporting the carbon from the carburizing medium proper (solid, liquid or gaseous) to the soft steel which it is desired to cement, until the concentration of the carbon in the cemented zone reaches a value such that it is exactly in equilibrium with that mixture of carbon monoxide and carbon dioxide which is in equilibrium with the carburizing agent under the given conditions. This last condition is strikingly realized when the cementation of the steel stops at the concentration of the carbon in the steel acting as carburizer, even when the two steels are not in direct contact.

In these examples, the specific action of the gaseous carburizing mixtures (to which *alone* the equilibrium phenomena observed can be referred) is so evident that it is no longer possible to doubt the very great preponderance of the *direct* action of the carburizing gas in comparison with the direct action of the carbon in contact with the steel or which may be deposited on the surface of the steel as the result of the decomposition of the gas.

The principles which I have developed also allow an explanation of some older observations already referred to. Thus, for example, we easily see the weakness of Mannesmann's reasoning which I have cited on p. 18, based on the alleged absurdity of admitting that the same gas contained in a crucible can on the one hand remove the carbon from the cast iron to yield it on the other to the steel. It is, in fact, quite understandable that a given mixture of carbon monoxide and carbon dioxide should act as an oxidizer on the carbon of the iron-carbon mixed crystals of high carbon content (of the cast iron) and as a carburizer on the mixed crystals of lower carbon content (soft steel). I have already reported the results of experiments which realize very simply and surely just the process considered as absurd by Mannesmann, producing, simultaneously and in the same operation, the decarbonizing of a cast iron and the cementation of a steel.

The same principles explain in a very simple way the phenomenon observed by Forquignon, of the refining of a cast iron ignited in carbon powder, and "therefore subjected to the same treatment which gives rise to the carburization of steel." In fact, my own direct experiments show that certain types of cast irons can be decarburized easily by gaseous mixtures with carbon monoxide as base which are in equilibrium with free carbon.

Finally, I wish to mention the results of some experiments which, on account of their essentially practical interest,[1] I shall examine more in detail in the second part of this volume.

These experiments show that when the cementation with mixtures of carbon monoxide and carbon dioxide in chemical equilibrium with free carbon (for example, with wood charcoal) is carried out under the usual experimental conditions which I have indicated, diluting the gaseous carburizing mixture with nitrogen, there are obtained cemented zones in which the maximum concentration of the carbon is less than that which would be obtained by working under identical conditions but without diluting the gaseous mixture. I shall consider in a subsequent chapter the theoretical and practical importance of this fact.

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[1] F. Giolitti and G. Scavia, *Sull'impiego dei forni a muffole orizzontali nella cementazione dell'acciaio coi cementi misti* (*La Metallurgia Italiana*, August, 1911).

CHAPTER V

THE PRESENT STATE OF THE THEORY OF THE PROCESS OF CEMENTATION[1]

The simple setting forth in the preceding chapters of the theoretical conclusions resulting from the experimental investigations carried out to determine the nature of the process of cementation define the actual state of our knowledge on this subject. It does not, however, seem to me useless to further summarize and briefly classify this knowledge, and to show how the inconclusive and at times apparently contradictory results of the first experimental investigations are clearly explained by results of more recent investigations. This will place still better in evidence the real value of the most recent studies, showing that the experimental foundation of the new theories is considerably more extensive than that on which they were directly constructed.

One of the questions which has been discussed at greatest length and with the greatest interest is the part played in the process of cementation by the various carburizing gases, especially as compared with the *direct* action of the free carbon. And here, it seems to me, one of the prinicipal causes of the discordance of opinions must be sought in the fact that in many cases the various experimenters set themselves, in reality, quite different problems, which could not admit of a common solution. It is easy to see this by examining, for example, the experimental data discussed by Ledebur and by Guillet in their polemic, which I reviewed at length in the preceding pages. Thus, for example, Guillet, among other things, proposed to show that pure carbon, *in the absence of the smallest trace of gas*, can not cement iron, but he admitted explicitly that in industrial practice the carbon monoxide produced by the oxygen of the air contained in the cementation boxes on the carbon of the cement may give rise to a cementation, though "very slow." Now, given this premise, it can not but cause surprise to see Ledebur oppose to Guillet, in proof of the possibility of producing the cementation directly with solid carbon without the intervention of any gas, experiments carried out without the least precaution for eliminating from the medium in which the cementation is effected precisely that gas (air) to which Guillet had, at least partially, attributed the cementation. This fact, otherwise inexplicable, is easily explained when we note the fundamental difference between the problems which each of them proposed to solve. While Guillet proposed to establish, *as a scientific datum*, the fact that pure carbon can not cement iron when the presence of the slightest trace of gas is excluded, Ledebur wished simply to prove that under the ordinary conditions used in industrial practice, the intervention of the special gaseous compounds named by Guillet (volatile cyanides, carbon monoxide, etc.) need not be considered necessary to obtain a good *technical* result. This explains also the insistence of Ledebur in reproaching Guillet for not having carried out his experiments on a large scale under the conditions of industrial practice; such a reproach would evidently be considered absurd and ridiculous by one approaching the problem from the purely scientific point of view of Guillet.[1]

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[1] The contents of this chapter have already been published in part in a note which appeared in September, 1911, in the *Rassegna Mineraria, Metallurgica e Chimica.* In the present compilation, however, have been added various considerations relative to many researches carried out since that time.

Analogous observations could be made on the polemic between Caron and Margueritte, on the cementing action of carbon monoxide.

Granting this point of view, let us examine briefly, on the basis of the more recent experimental data, the conclusions of various experimenters on the function of the various gases in the process of cementation.

Leaving aside, because of its evident improbability, Laurent's hypothesis (see p. 4), according to which the cementation is due to the action of the vapor of carbon on the iron, we find as early as 1841 the theory of Leplay attributing to carbon monoxide the principal part in the process of cementation with wood charcoal. We have further seen that this hypothesis, slightly changed in form by substituting the conception of continuous reactions tending to a definite state of equilibrium, for that of alternating complete reactions, is in substance fully confirmed by the recent investigations, detailed in Chapter IV. These have shown, in fact, that in the great majority of processes of cementation used in practice the reaction which greatly predominates over any other is carbon monoxide acting as "vehicle" for the diffusion of the carbon into the mass of the steel. But the hypothesis of Leplay was not founded on sufficient known experimental data, and the criticisms by Gay-Lussac five years later (see p. 4), cautioning against the acceptance of hypotheses not based on direct and sure experimental proofs, were perfectly justifiable. The criticisms of Gay-Lussac were the incentive to a long series of experimental investigations, which have only in the last few years led to sure conclusions.

[1] I consider it, in general, absolutely unjustifiable to assert that the course of an industrial process can be cleared up *solely* on the basis of the results of experiments on an industrial scale. In fact, laboratory investigations, if chosen and carried out along proper and interpreted rationally, constitute the most valid means (and in many cases the neans) of clearing up the course of very complicated processes, whether industrial Such alone permit of *isolating* the elementary phenomena constituting a complex nenon, whose very complexity would render it inaccessible to *direct* investigation. is reason I believe that the ideas expressed by Mannesmann (see p. 15), by Ledebur 60), and by others concerning this subject must be regarded as beside the mark.

Among all the various groups of gaseous carburizing compounds, that to which the majority of experimenters attributed the greatest efficacy in the process of the cementation of iron is without doubt the group comprising cyanogen and its derivatives, and especially the volatile alkali cyanides.

That cyanogen and the more or less volatile cyanides can cement iron intensely is beyond doubt. It is sufficient, to prove it, to note the results of the cementation experiments carried out by Caron, using pure ammonium cyanide (see p. 6). Moreover, it is well known that fused potassium cyanide and potassium ferrocyanide are used in the pure state to obtain thin and strongly carburized cemented zones in the case-hardening of machine parts.

But it is inexplicable why accurate experimenters, such as Caron, Guillet and others, observing merely that the isolated alkali cyanides or ammonia in the presence of carbon (see p. 5) can cement iron, inferred directly that cyanides always play the chief part in the carburizing action of the cements in the cementation industry. In industrial practice the cyanides do not exist already formed, but may be formed in very small quantity by the action of the nitrogen of the air (occluded in the cement) on the carbon used and on the small quantities of alkali constituting a part of the ashes of this carbon. Although the formation of small quantities of alkali cyanides can not therefore be wholly avoided in industrial cementation with carbon as base, the part which is played by these traces of volatile cyanides is *certainly negligible* in comparison with that of the carbon monoxide formed by the action of the oxygen of the air on the carbon used as cement. The following facts show certainly and clearly the correctness of this assertion:

1. If the activity of cements with carbon as base were due essentially to cyanides formed by the action of the nitrogen of the air occluded in the carbon on this carbon and on the alkalis contained in its ashes, it is evident that the intensity of the cementation should be greatest when the cement is made to act in an atmosphere of nitrogen, and least when a gas *free from nitrogen*, as, for example, carbon monoxide, is completely substituted for the air occluded in the carbon. But our experiments (see p. 121) have clearly shown the contrary, *viz.*, that wood charcoal in an atmosphere of pure nitrogen gives rise to only a very faint carburization of the iron, while this same carbon, freed from the last traces of occluded nitrogen by repeated ignitions in a current of pure carbon monoxide and kept, before and during the cementation, in an atmosphere of pure carbon monoxide, gives very intense cementation. Thus, from numerous experiments it has been proved that the carburization is considerably more intense when the carbon is made to act on the iron in an atmosphere of carbon monoxide freed from nitrogen than when it is made to act in the presence of air, in which case the nitrogen intervenes together with the carbon monoxide.[1]

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[1] Charpy also (see p. 113) observed an analogous phenomenon, but his observation is more than a year later than some patents of mine in which this phenomenon is clearly

2. We are led to the same conclusion by discussing the cementations carried out by Ledebur (see p. 61), using carbon whose ash did not contain alkalies capable of forming volatile cyanides.

3. From the experiments of Charpy (see p. 113) it follows that in the majority of cases, using cements with carbon as base, not the least trace of cyanides is formed during the cementation, and this, too, in cases in which the carburization is most intense. Thus, for example, using the cement of carbon powder and barium carbonate, no traces of cyanides appear except at temperatures higher than 1050° C., while the carburizing action of this cement is very intense even at a much lower temperature. It is to be noted that it was particularly on a consideration of the activity of this cement that Caron and then Guillet based their hypothesis of the necessity of the intervention of cyanides in the cementation.

4. Numerous experiments (see pp. 78–81) show that pure hydrocarbons, and especially those freed from the smallest traces of nitrogen, strongly cement iron. This, moreover, Caron himself had been forced to admit, on the basis of his own experiments carried out to confute the theories of Frémy (see p. 7). But Caron maintains that with hydrocarbons there is not obtained true cementation proper, since they always furnish cemented zones so strongly carburized as to constitute true cast irons, not steels. This last assertion, however, does not correspond to the facts, as is clear from a large number of experiments on this head which I have summarized in the preceding chapters.

The only consideration which can justify attributing to cyanides the carburizing action of cements with carbon as base is the double assumption that carbon can not cement the iron directly without the intervention of a gas, and that carbon monoxide has no cementing action whatever on the iron (Caron) or only a very slow and practically negligible carburizing action (Guillet). Admitting the necessity of the intervention of a carburizing gas and excluding the possibility that this gas could be carbon monoxide, it must be recognized that the simplest hypothesis was that of attributing the carburization of the iron to the action of volatile carburized compounds of nitrogen, especially as

described. Moreover (as I have already pointed out) not all of Charpy's observations in this memoir are entirely correct. It suffices, for example, to cite those (see *Revue de Métallurgie*, 1909, p. 517) on the different behavior of the carbonates of calcium and barium, from which it almost seems as if the author attributed to the different nature of the two carbonates the different proportions of carbon dioxide and of carbon monoxide which are evolved in their mixtures with carbon. So, too, the observation contained in the note on page 518 of the same memoir on the "limitation" of the cementation carried out in a limited atmosphere of carbon monoxide holds only when the steel subjected to the cementaion is in wires or thin plates or in small granules; for we know that in ordinary cases, in which pieces of iron of medium or large dimensions are cemented, even in a limited atmosphere of carbon monoxide, the cementation can reach a great depth (theoretically unlimited), but with the *concentration* of the carbon in the cemented zone becoming continually smaller.

it had already been proved that not only cyanides already formed but even dry ammonia in the presence of carbon can cement iron. Nevertheless, as we have seen in the preceding chapter, there not only was lacking any direct proof of the new hypotheses, but more recent experiments have since shown that both of the assumptions made the basis of these hypotheses are absolutely without foundation—especially the second, relative to the impossibility of practically cementing iron with carbon monoxide. At present, the action of carbon monoxide suffices to explain perfectly the processes of cementation which earlier experimenters thought it necessary to explain by the intervention of cyanides.

We must however explain the numerous negative results obtained by various experimenters in attempts to show the carburizing action of carbon monoxide on iron.

The first precise experimental investigations to establish whether carbon monoxide can cement iron were those carried out by Caron and by Margueritte in the course of the discussion to which I have already referred.

Caron in all his experiments used specimens of iron of considerable dimensions,[1] and to determine the amount of cementation he contented himself with breaking the specimens, after having forged and hardened them, and examining the "grain" of the fracture. Now, my recent experiments (see p. 78) show that, working under these conditions, and especially if the temperature of the cementation is high and the quantity of carbon monoxide used is not very large, or the gas is not absolutely pure, there are obtained, without the intervention of the slightest traces of cyanides, quite deep cemented zones, but the concentration of the carbon in them is too small to make it possible to recognize the cemented zone from the simple appearance of the surface of fracture.

That this is the cause of Caron's error is proved by the fact that he himself admitted that carbon monoxide can cement iron at dark red heat,[2] but not (contrary to the assertions of Margueritte) at the higher temperatures at which the industrial process of cementation is always effected.[3] We have seen that the knowledge acquired more recently about the conditions under which the process of cementation is effected by means of carbon monoxide permits of asserting that in the cementation of specimens of considerable dimensions with carbon monoxide alone the essential difference between the product which is obtained by working at a low temperature (700–800° C.) and that which is obtained at high temperatures (1000–1100° C.) consists chiefly in the *concentration* of the carbon in the cemented zones, a concentration which is the smaller the higher the temperature.[1]

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[1] In general 10 × 10 × 300 mm., dimensions much greater than the mean thicknesses of the carburized zones which are obtained with the usual cements working under the conditions of length and temperature adopted by Caron.

[2] Wedding also (*Ausführliches Handbuch der Eisenhüttenkunde*, Part 2, Vol. IV, p. 237) asserts that carbon monoxide does not cement iron except at temperatures *below* 400° C. On the basis of this, and other considerations on the exhaustion of the gases of the cementation boxes, Wedding holds that in practice the gases can at most but "initiate" the cementation.

[3] It is clear from what I have said that in the discussion between Caron and Margueritte there occurs a misunderstanding analogous to that between Guillet and Ledebur, already described. We have seen how this misunderstanding was due essentially to the fact that one of the experimenters considered and studied the process of cementation exclusively from the point of view of its technical applications, the other from the scientific standpoint.

This explains the error of Caron, who, however, also reasoned erroneously that because carbon monoxide *alone* does not (as he thought) cement iron, the action of the carbon monoxide is *nil* even in the cementation boxes, where it is in the presence of an excess of carbon. Now, we have already seen on p. 135 that in the presence of the free carbon the carburizing action of the carbon monoxide is modified, becoming more intense, so that it can be used directly in practice with great advantage.

Caron evidently was misled by his premature conclusion when, on the basis of a direct experiment, he asserted that carbon monoxide even in the presence of carbon can not cement iron. In fact, numerous experiments prove the contrary, and the wide technical applications of the carburizing activity of carbon monoxide used together with carbon allow no doubt as to the error of Caron.

To analogous experimental errors must be attributed the assertion of Saunderson, cited by Caron in support of his hypothesis (see p. 6), that the cementation is effected *only* by the simultaneous action of nitrogen (for example, in the form of ammonia) and of carbon, and that, for example, carbon monoxide and ethylene, taken separately, can not cement iron.

Contrary to Caron, Margueritte in his cementation experiments with carbon monoxide always used the iron in the form of thin pieces such as wires, or thin sheets, or filings, or powder obtained by the reduction of iron oxalate. Only in one case did Margueritte use a bar of iron 6 mm. thick. These are thin compared with the thicknesses of cemented zones obtained with the usual cements, working under the same conditions.

Now, under these conditions the carbon yielded by the carbon monoxide can not diffuse deeply into the mass of the iron, as takes place when specimens of iron of greater dimensions are cemented. In the latter case, as I have already explained, the carbon monoxide lowers the concentration of the carbon at the periphery of the cemented pieces, functioning as a "vehicle" for the rapid diffusion of this carbon toward the deeper parts of the specimens. It is evident, therefore, that when the surface of the iron subjected to cementation is considerable as compared with its mass, the concentration of the carbon in the metal can more quickly reach a high value.

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[1] The same consideration serves to explain clearly the apparently strange observation of Charpy (see p. 45), according to which "the velocity of the cementation" with carbon monoxide does not increase sensibly for temperatures higher than 900° C. In reality, "the velocity of cementation"—meant as "depth reached by the cemented zone in a given time"—increases with increase in the temperature even much above 900° C., and my more recent experiments (see p. 78) show it clearly. But, given the conditions under which Charpy worked (see the observations made on page 46), the decrease in the *concentration* of the carbon which, for the reasons which I have indicated, gradually manifests itself as the temperature rises above 900° C. is such that the *quantity* of the carbon absorbed in a given time (for a given velocity of the current of carbon monoxide) continues to diminish with rise in the temperature.

This explains how Margueritte, contrary to Caron, obtained cementation with carbon monoxide, even when working at high temperatures.[1]

Margueritte also made some observations which have been clearly confirmed by more recent experiments and the physico-chemical theory of cementation with carbon monoxide. Thus, he observes that in iron wires cemented with carbon monoxide, all other conditions being equal, the concentration of the carbon is the smaller the higher the temperature (between cherry-red and orange-red) at which the cementation was effected. Later he himself properly pointed out that Percy in 1859 had used too small quantities of carbon monoxide to obtain appreciable cementations. This is confirmed by our own results.

Summing up, I believe it can be asserted that the observations of Margueritte, examined in the light of our present knowledge, constitute an excellent refutation of the hypothesis of Caron regarding the necessary and preponderant intervention of cyanides in industrial cementation, and substantiate the active carburizing action of carbon monoxide and of carbon alone on iron.

Other experimenters also, finding that carbon monoxide, acting *alone* on the iron, gives carburizations of slight intensity, or, more correctly, cemented zones of low carbon content, held that in cementation with cements having carbon as base (such as are used in industrial practice) the specific carburizing action of the carbon monoxide was by far less intense than the direct action of the carbon or of the other gases (cyanides, nitrogen, etc.). Their mistake consisted in not knowing that the carburizing action of the carbon monoxide is strongly "intensified" by the presence of the carbon.

In this connection I will also recall the conclusions of Mannesmann (see p. 17). Boussingault pointed out that the quantity of carbon monoxide which can be formed in the ordinary cementation boxes would be sufficient to cement only a very small part of the 13 or 14 tons of steel contained in a box, but we have seen that more recent investigations have proved that under these conditions the carbon monoxide is not exhausted during the cementation, and really constitutes a most efficient vehicle in producing the diffusion of the carbon from the wood charcoal into the mass of the steel.

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[1] The same considerations also explain how Charpy (see page 45), cementing iron *wires and filings* with carbon monoxide, obtained strong carburization at high temperatures (1000° C.).

Guillet also (see p. 47) holds that the carbon monoxide which is formed in the cementation boxes (either by the action of the oxygen of the air on the carbon or by the action of this carbon on the carbon dioxide of the carbonates added to the cement) has an action which is but very slow and entirely secondary in the process of industrial cementation. But these considerations of Guillet, also, have been shown to be inexact.

Le Chatelier, even after the decisive experiments of Charpy, limits himself to observing that it is "difficult to admit that the cementing action of carbon monoxide is *nil*." Later, Bruch (see p. 66), on the basis of new experiments, affirms that carbon monoxide can not cement iron.

All these results, partially or totally negative, are explained by the considerations which I advanced in connection with the analogous results of Caron's investigations.

Assuming this, and having established by experimental data that in the ordinary processes of cementation with cements having carbon as base the action of cyanides is not preponderant but is entirely or almost entirely negligible, while the specific action of the carbon monoxide predominates, let us see how the results of the experiments which led to the hypothesis of the preponderant action of cyanides are explained. I shall refer to only two series of more noteworthy facts, for the examination of all these experiments would be long and tedious.

First of all, it is clear that the greater carburizing activity obtained by adding to the wood charcoal the carbonates of the alkali or alkaline earth metals (see, for example, Caron, p. 6, Guillet, p. 49) is explained perfectly by the results of the recent experiments showing the efficacious action of carbon dioxide. This is especially evident for the "inexhaustible" cement, composed of mixtures of carbon and of barium carbonate, proposed repeatedly, for example, by Caron and by Guillet. For this result, the agency of considerable quantities of carbon dioxide is evident, and this not only when the cement is used the first time but also every time this same cement, after having been used, is allowed to stand in contact with air before using again, so as to make possible the "regeneration" of the barium carbonate.

The other hypothesis, evidently untenable since the demonstration of the negligible part played by cyanides in ordinary cementations, is that first advanced by Caron (see p. 11) and then by Guillet (see p. 50), which attributes the "exhaustion" of the cements with carbon as base to the progressive volatilization of the alkali cyanides.[1] It is quite probable that the cause of this "exhaustion" is not a single one, so that it would be necessary to seek it along different lines, case by case, depending on the composition of the cement considered. It is indeed possible that in some cases the exhaustion may be due (as Margueritte and Mannesmann had already supposed) (see p. 19) to a change in the state of agglomeration of the carbon contained in the cement. This appears the more probable, now that we know the importance of the part which carbon monoxide plays in the cementation, when we consider the fact, demonstrated by Schenck, that with variations in the nature of the carbon its manner of acting with mixtures of carbon monoxide and of carbon dioxide also varies markedly, and this not only as regards the velocity of the reactions but also as regards the final conditions of equilibrium to which these reactions lead.[1]

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[1] The persistence observed by Guillet in the carburizing action of the carbon in the presence of ammonia can certainly be due to the formation of ammonium cyanide. But here also (analogously to what I have already pointed out on p. 171 of the present chapter) this *in no wise* proves that the exhaustion of the cements is due to the volatilization of the cyanides, whose presence or formation in these cements is, moreover, negatived by the experiments of Charpy.

For cements containing easily fusible alkali carbonates and cyanides, it is not improbable that to the causes just indicated there may be added a diminution in the "reacting surface" of the porous carbon, due to the fact that the latter becomes impregnated with the fused salts.

Having now cleared up some of the fundamental points of the theory of cementation, the discussion of which required more detailed consideration, let us try to draw some concrete conclusions from the results of the various experiments described, especially concerning the conditions which are present in practice, on the *direct* cementing action of carbon in ordinary industrial cementation.

And here it is, first of all, necessary to put the matter very clearly, in order to avoid drawing opposite conclusions from the experiments of various experimenters.

Here, put in the most schematic form, are the various partial questions to which the experimental researches of the group with which we are dealing may furnish an answer. Together with each question I add, in succinct form, the answer which can be given to it by the numerous experiments which I have cited in the preceding pages. A few brief references to the facts already developed will then suffice to show how the conclusions correspond well with all the experimental results obtained by the various experimenters.

1. Can *carbon alone*, simply heated in contact with solid iron and without the intervention of any gas, carburize iron?

This question, of a purely scientific character, experiment answers affirmatively.

2. Can *carbon alone*, that is, simply heated in contact with solid iron without the intervention of any gas, give rise to cementation of practically suffi-

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[1] Moreover, when we take into account the various facts which I have cited concerning the manner in which carbon monoxide intervenes in the processes of cementation, it is easily understood how a cement formed of practically pure carbon (such as sugar carbon) must be rapidly exhausted owing to the fact that the small quantity of carbon monoxide which can be formed at the expense of the oxygen of the air occluded in it is eliminated either because a part of it passes into solution in the iron or because another part escapes from the cementation boxes, the joints of which are always permeable to gases.

cient intensity under the conditions of time and temperature which are ordinarily present in industrial practice?

This question, of an essentially technical character, experiment answers negatively. The cementation obtained with carbon *alone*, in the absence of any gas, is of practically negligible intensity.

3. What part does the carbon and what part do the gases play in the ordinary processes of cementation used industrially?

To this question it is not possible to give a single answer, holding for all cases. It is necessary, for every type of cement, to examine the specific carburizing action of the gases which may be formed in its use, and to study in what way this specific action is modified by the presence of the free carbon pre-existing in the cement (as, for example, in the cement composed of the mixture of carbon and barium carbonate), or formed during the cementation (as, for example, in the cementation carried out in the presence of hydrocarbons).

I shall examine later from this point of view some of the cases which occur in practice, to show the real technical value of these recent studies.

Beginning with the first of the three questions enunciated above, we can affirm that the fact that carbon *alone*, without the intervention of any gas, cements the iron with which it is kept in contact for a sufficiently long time and at a sufficiently high temperature has been proved with certainty by a number of the experiments which I have described in the preceding chapters. Among the most convincing are those of Mannesmann (see p. 18), carried out with cast-iron turnings "drowned," together with the iron specimens, in fused salt or lead, in which case the exceedingly slow cementation of the iron specimens takes place only at the points at which they come in contact with the cast iron. We can also refer to those of Roberts-Austen (see p. 27), in which the carburization of pure electrolytic iron by the action of a diamond placed in contact with it was effected at bright red heat *in a vacuum*, and after both the iron and the diamond had been ignited for a long time in a vacuum to totally eliminate occluded gases from them. Royston's tests (see p. 30) proved that the carbon diffuses from a piece of highly carburized steel (0.95% C) to one less carburized (0.15% C) with which it is kept in contact *in a vacuum* at a high-temperature, and that diffusion ceases as soon as there is no longer *direct* contact between the two specimens of steel. Arnold and MacWilliam (see p. 34) proved the diffusion of carbon from a more highly carburized steel to one less carburized kept in intimate contact *in a vacuum* at a high temperature.[1] The same was proved by more recent experiments carried out by myself and Astorri (see p. 121), by Guillet and Griffith (see p. 122), and by Weyl (see p. 124).

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[1] In truth, the experiments of Royston and those of Arnold and MacWilliam (contrary to those of Mannesmann and of Roberts-Austen and the more recent ones) do not furnish a *direct* proof that *free* carbon can cement iron without the intervention of any gas, but only show the fact, which is not entirely equivalent, that the intervention of any gas is not necessary to produce the diffusion of the carbon from one point to another in a mass of solid steel. Really this last process is but one (though the most important one) of the two phases of the process of cementation.

On the other hand, experiments based on the observation that when carburizing gases are not totally eliminated or absent the cementation is always more intense at the points at which the carbon is in direct contact with the iron have but little evidential value; such are, for example, the experiments carried out by Margueritte with diamond and graphite powder in a current of hydrogen (see p. 8), by Percy (see p. 13), by Mannesmann (see p. 18), by Bell, etc. This is so because experiment shows (see p. 138) that the various gases, and especially that one which acts most efficaciously in cementation, *viz.*, carbon monoxide, act with maximum intensity in the immediate proximity of the free carbon, and their carburizing activity diminishes when the distance between the point at which the carburization of the iron is effected and that at which the gas can be regenerated by reacting with the free carbon increases. This diminution in intensity, which is quite slow when the gas can move freely between the surface of the steel and the carbon which must regenerate it, becomes very great when these movements are obstructed and the carbon is far from the surface of the steel; this happened, for example, in the experiments of Mannesmann cited, in which the surface of the steel not in contact with the carbon was buried in refractory earth, in whose pores the gas circulates only with extreme slowness. Next, the experiments of Ledebur (see p. 60), carried out on a large scale but without care to eliminate the gases occluded in the carburizing powders used for the cementation, prove absolutely nothing when the problem is considered from the more general scientific point of view.[1]

Taking up the second question and the answer given, it follows from the same experiments which I have cited above that the "direct" carburizing action of free carbon on the iron, by simple "contact" at a high temperature, acting alone and without the intervention of any gas, if not null,[2] is at least certainly *exceedingly small.* As to deciding whether this *direct* action of carbon on iron, in the absence of the slightest traces of gases, is *really absoutely null* or only extremely small, the information may present a certain interest from the theoretical point of view but it is a problem of very small, if of any, practical interest.[1]

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[1] The small scientific value of these experiments of Ledebur is still more evident now hat we know the efficacy of the intervention of the oxygen of the air occluded in the cements as a generator of carbon monoxide). Guillet did not succeed in showing this in his atempt to point out that Ledebur had not eliminated the possibility of the formation of lkali cyanides, to which chiefly and almost exclusively he attributed the process of ementation.

[2] Charpy and Bonnerot consider it null, on the basis of the results of some of their ecent experiments (see *C. R. de l'Académie des Sciences*, 1st sem., Vol. CL, p. 173). Charpy bserves that the fact that temper-carbon redissolves in the iron as the result of prolonged eating (a fact which Le Chatelier (see p. 64) had cited as proof of the possibility of the *irect* diffusion of carbon into iron) may be due to the action of the gases always present in olution in the iron. He holds that "solid carbon outside of a fragment of steel can not enetrate into it without the intervention of a gaseous vehicle."

On the other hand, the solution of the third question which we have set ourselves presents a very great practical as well as theoretical importance. This is the establishment of the part played directly in the process of cementation by the various gases and that played, directly or indirectly, by the free carbon when the gases and the carbon act simultaneously, and in what way the two groups of substances (the solid cement with carbon as base and the gases), acting simultaneously, reciprocally modify each other's specific action.

To treat such a complex problem it is first necessary to examine, at least briefly, the behavior, in the presence of iron and of free carbon, of the individual gases which may be active in the processes in practical use. And, indeed, this examination furnishes the answer to our question for the most frequent cases.

Of the gases which may take part in cementation carried out by the usual processes, let us begin by considering free nitrogen. In all cementations carried out with solid cements there is necessarily present the nitrogen of the air contained in the cementation boxes.

We have already seen (see p. 7) how Frémy's hypothesis that nitrogen acts *directly* on iron, simply "nitrogenizing" it and transforming it into steel, was quickly shown to be false by the experiments of Caron.

Later (see p. 26), Hempel maintained, on the basis of careful experiments, that carbon in the presence of pure nitrogen freed from the smallest traces of oxygen can not cement iron. Considerably more recently, Le Chatelier (see p. 58) held that in the usual processes of cementation nitrogen is the agent which transports the carbon into the mass of the iron. In reality, all the more recent and more precise experiments show that during cementation the nitrogen may diffuse in small amounts into the iron (see p. 139). This may be the cause, as Le Chatelier suggested, of the increase in brittleness sometimes observed in those parts of the steel subjected to cementation which the carburization had not even reached. It is however now certain that the presence of pure nitrogen does not increase except to a minimum extent the carburizing action of free carbon. The cemented zones which are obtained by the simultaneous action of carbon and nitrogen are in particular (see p. 121) characterized by a very low carbon concentration.[2] The explanation of this

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[1] For this reason it seems to me that there is no justification for the observation of Guillet, who, in reporting some of his communications presented before the Congress of Metallurgy of Düsseldorf (see *Bull. de la Soc. des Ing. Civils de France*, October, 1910), asserts that it would be of extraordinary importance for technology to establish with certainty whether carbon alone can cement iron without the intervention of gases.

[2] This explains, when we consider my explanation of the erroneous conclusions drawn by Caron in connection with the carburizing action of carbon monoxide, why Caron asserted that carbon in an atmosphere of pure nitrogen can not cement iron.

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last phenomenon, which is the cause of the negative results obtained by Hempel, is the fact that the intervention of nitrogen in the process of cementation must be explained in a manner analogous to that of carbon monoxide, that is, by a reaction whose final equilibrium depends also on the concentration of the carbon dissolved in the iron of the cemented zones. But, while the reasons for the specific carburizing action of the carbon monoxide, alone or in presence of free carbon, have been accurately studied and are now known in all their particulars, the reactions (certainly analogous) to which the slight specific carburizing action of nitrogen in the presence of the free carbon is due have been studied considerably less, and we have no precise data about them.

For practical purposes this deficiency in data about the specific action of nitrogen has no importance, for exact experiments have shown that in the technical study of the processes of cementation we do not have to take into account the intervention of the free nitrogen, whose action in the presence of free carbon is certainly too slight to influence practically the results which are obtained with a given cement.

With a second class of volatile carburizing compounds, the cyanides, I have already dealt, in discussing whether the volatile cyanides take a preponderant part in the ordinary processes of cementation. I there showed by rigorous experiments that these cyanides (which, without doubt, exercise on iron at a high temperature an intense specific carburizing action) are never formed in the cements usually employed, or that they are formed only under special conditions, but always in such small amount as to render their action practically negligible. As to those special cases in which solid or fused cyanides or ferrocyanides are used directly for the cementation of steel, alone or mixed in considerable proportions with other carburizing substances, it is certain that their intense specific action is exercised directly on the iron, adding itself to that of the other carburizing substances. In these cases also, therefore, the intervention of the cyanides *as volatile gases* at the temperature of the cementation is absolutely negligible.

We conclude, therefore, that in the examination of the respective parts played by the gases and the free carbon in industrial cementation we need not take into account the cyanides, because experiment shows that these, when they intervene as gases or vapors, produce only a negligible effect. As to the intense action of the solid or fused cyanides, this in no way concerns the part of the problem we are now considering.

Among the gases which usually and efficaciously act in industrial cementation with free carbon are the hydrocarbons. Such gases are really widely used in practice for every kind of cementation from thin cementation of machine parts up to the deepest cementations, such as those which are used for armor for ships. In almost all these cases (see p. 114) a part of the hydrocarbon used for the cementation is decomposed, setting carbon free. Therefore, both in the case in which the hydrocarbons are used alone and where they are introduced into the cementation boxes (or are formed there by the decomposition of organic substances), in the presence of pre-existing free carbon, we have the problem of establishing what part is played by the direct action of the gases and what by the action of the free carbon which they deposit on the surface of the iron.

And here it is well to make clear what is meant by the *action of the gases* in cementation. Any carburizing gas whatsoever can cement iron only by the action of the carbon which it can set free in decomposing. But this separation of free carbon can take place in two distinct ways:[1]

1. The gas may decompose totally as soon as it comes in contact with the surface of the steel, setting free on this surface all the carbon which it is capable of yielding. In this case it is evident that the carburizing gas exercises no other function than that of carrying the carbon into intimate contact with the steel. As to the process of the cementation proper, or the more or less deep diffusion of the carbon into the mass of the solid steel, this is effected in this case exclusively by the solution of the carbon in the surface layer of the steel and its passage from this layer to the succeeding one through the action of one of those processes of diffusion *by difference in concentration* which have been observed in a large number of alloys formed of solid solutions.[2]

In these cases we properly say that the gas exercises no specific action on the course of the cementation. It may also be asserted that this extreme case never presents itself in practice.

2. The gas may decompose only partially when it comes in contact with the surface of the steel, setting free there only a part of the carbon which it is capable of yielding. The gas, then, as it diffuses into the mass of the steel continues to decompose, setting free in these interior layers of the steel new quantities of carbon which gradually pass into solution *directly* in the metal of the deeper and deeper layers.

In this case, which we have seen occurs with special clearness in the case of carbon monoxide, we say that the gas exercises a direct specific action on the course of the cementation. In this case, all the variations in the conditions (for example, the pressure, the quantity of the gas, etc.) on which the diffusion of the gas into the steel depends or the reaction by which the gas can set carbon free must greatly influence the course of the cementation.

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[1] See also the observations of Le Chatelier (p. 64).

[2] It is interesting to recall in this connection the results of the investigations of many experimenters on diffusion in other metals. I have already referred to the investigations of Roberts-Austen on the diffusion of gold and of platinum into lead, on the basis of which he asserted the complete analogy between these and the process of cementation. The latter would therefore be a simple phenomenon of direct diffusion of the carbon into the iron by difference in concentration

In reality, the "concentration-depth" curves determined by Roberts-Austen for the two pairs of metals Au-Pb and Pt-Pb differ profoundly from the analogous curves which I have reproduced in the preceding pages for the processes of cementation, and especially for those of them based on the action of carbon monoxide. This is explained by the direct action of the carburizing gases and thus constitutes a new proof of their intervention.

In the case of the hydrocarbons with which we are now dealing, there is no doubt that a part of the carburizing action which they exercise on iron at a high temperature is due to the *direct* action of the carbon which they always deposit on the surface of the metal. In fact, we have seen that solid carbon heated in contact with iron cements it, even without the intervention of any gas, and moreover it is quite probable that with pulverulent carbon in a state of extreme division, such as that which is formed in the decomposition of hydrocarbons, the direct action "by contact" is considerably more intense than with powdered wood charcoal, if for no other reason than the more perfect contact between the carbon and the surface of the steel.

But we have seen[1] that in cementation carried out with pure hydrocarbons both the depth reached by the carburization in a given time (velocity of cementation) and the maximum concentration attained by the carbon in the cemented zone increase markedly with increase in the *pressure* of the gas and in the *quantity* of this gas which comes in contact in a given time with a given surface of the steel. These facts show that in cementation with the hydrocarbons there is also a specific action of the gases, or that the diffusion of the carbon into the steel is due also to diffusion into it of the carburizing gases, which react with the steel in the deep zones, there yielding carbon directly. In fact, the variations in the velocity of the cementation and in the concentration of the carbon in the cemented zones can not be due to the free carbon which the gas always deposits in excess on the surface of the steel; for of this carbon the only part which can act directly by contact is that of the first layers formed immediately on the surface of the metal and not that further portion which, through an increase in the pressure or of the quantity of gas used, may eventually be deposited upon the preceding, without increasing the quantity of free carbon which is actually in contact with the surface of the steel.

This explains the expression of Guillet, that in cementation hydrocarbons certainly act "by dissociation" (see p. 48); and we can now say that the way in which hydrocarbons behave in the presence of iron or of free carbon is fully known.

Finally, another carburizing gas, which does not belong to any of the groups which we have just examined, is carbon monoxide. I have spoken at length of its great efficacy in the process of cementation, basing my remarks on the results of numerous experiments reported in the preceding chapters. I have also already spoken of the special manner in which carbon monoxide behaves as cement, either alone or in the presence of free carbon and of hydrocarbons.

First of all, we have seen (see p. 45) that carbon monoxide, acting alone on iron, deposits free carbon on it only at temperatures lower than those ordinarily used in industrial cementation, that is, below about 700° C. At all the temperatures used in cementation practice, carbon monoxide carburizes iron exclusively through its specific action *as a gas*, and this action is not modified by the deposition of free carbon on the surface of the metal, in a state of extreme division.

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[1] See p. 82 and especially the data contained in the tables on pp. 78–81.

This fact facilitates enormously the exact study of the characteristic specific action of carbon monoxide, not only in the case in which the carbon monoxide is made to act alone on the iron, but also in the case in which it acts together with other carburizing substances whose specific action is known.

I have already reported in detail the proof of the very slight and practically negligible carburizing action which the ordinary forms of carbon (such as wood charcoal, sugar carbon, etc.) exercise *directly* on iron in the absence of gases. This, with the facts just related, permit of stating at once that when the very efficacious cement composed of carbon monoxide and the ordinary forms of carbon (for example, wood charcoal) acts on the iron, the greatly preponderating action is the specific action of the carbon monoxide, modified and greatly "intensified," in the way which I have explained further back, by the presence of the free carbon.

The same observations show that the carburization obtained with carbon monoxide mixed with such a small proportion of volatile hydrocarbon that during the cementation the gaseous mixture can not set carbon free at the surface of the iron is due exclusively to the specific actions of the two gases; actions which in this case are additive, reciprocally modifying each other in the manner we have seen.

From the facts set forth and the considerations developed we can now draw these conclusions of practical interest:

1. The *direct* action of the carbon in the forms in which it is habitually used in solid cements is exceedingly slight; it is absolutely negligible as far as regards the *technical* results which are obtained with a given cement.

It is barely possible that the direct carburizing action of the carbon in a state of extreme division which some carburizing gases, such as the hydrocarbons, deposit on the surface of the steel may be of appreciable extent.

2. The salts derived from cyanogen (cyanides, ferrocyanides, etc.) exercise on iron a specific carburizing action, which has not yet been studied with precision. At any rate, the most reliable experiments show that, contrary to what various experimenters thought they had proved, the activity of cements containing free carbon and carbonates of the alkali or alkaline-earth metals is certainly not due to the formation of volatile cyanides by the action of the nitrogen of the air on the alkali or alkaline earth carbonates, but to the formation of carbon monoxide by the action of the carbon on the carbon dioxide produced by the dissociation of the carbonates.

3. The carburizing action of nitrogen in the presence of carbon is also technically negligible.

4. In the carburizing action on iron exercised by the hydrocarbons at a high temperature, there certainly occurs to a very considerable extent the *direct* action of the gases. However, experimental data are lacking which would establish the extent of the simultaneous direct action of the finely divided carbon which the hydrocarbons, in decomposing, deposit on the surface of the iron.

5. The carburizing activity of pure carbon monoxide on iron at the temperatures used in the practice of cementation is due exclusively to the direct specific action of the gas.

6. The specific carburizing action of carbon monoxide becomes most intense when the gas acts on iron in the presence of free carbon. This specific action, modified by the other carburizing substances present, such as hydrocarbons, cyanides, etc., is enormously preponderant above all the others in all cements in which carbon monoxide is present or can be formed,[1] among which must be numbered all the most widely used solid cements.

Besides wood charcoal, which we have shown to act exclusively through the action of carbon monoxide, the "inexhaustible cement," first proposed by Caron and then by Guillet and used to-day very frequently for the superficial cementation of machine parts, acts similarly. To the same group belong the cements derived from the last mentioned by substituting wholly or partially for the barium carbonate other carbonates, such as the carbonate of calcium, of sodium, of potassium, etc.

Finally, the cements based on the use of pure carbon in a current of carbon monoxide, pure or diluted with nitrogen, belong to the same group, their activity being due exclusively to the specific action of carbon monoxide.

The carburizing substances containing cyanogen (such as the alkali cyanides, the ferrocyanides, etc.), are at present limited in use to operations of secondary importance, for which the exact knowledge of the way in which the diffusion of the carbon into the steel takes place presents little or no interest. In fact, we shall see that they are used in those cases in which a very hard metallic surface is needed and it does no harm if the cemented zone is very thin and, after the hardening, brittle. Aside from these, only two classes of carburizing substances act directly in all the processes of cementation to-day used industrially:

The first class includes the volatile hydrocarbons, whose specific carburizing action is strongly in evidence when they are used alone, and also in those processes in which they act together with free carbon or other solid carburizing substances.

The second class includes carbon monoxide, whose specific action is greatly preponderant in almost the whole of the cements used to-day in practice.

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[1] This shows the inexactness of the opinions of the various experimenters who considered the carburizing action of carbon monoxide in the processes of cementation negligible as compared with that exercised directly by the carbon or by other carburizing gases or vapors.

It is evident, therefore, that a physico-chemical theoretical study of the process of cementation, whose final and essential object must be to establish precise rules for the practical conduct of the industrial process, must establish first of all the behavior, either alone or in the presence of the ordinary forms of compact carbon, of the two classes of carburizing substances just mentioned. The results of such a study will also furnish practically all the data necessary for the conduct of the actual processes of cementation for we have already seen that the action therein of all the other substances present is practically negligible.

For the case of the hydrocarbons, we may represent schematically the general reaction to which their carburizing effect on iron is due as follows:

$$C_mH_n = C_{m-x}H_{n-2y} + yH_2 + xC.$$

The course of the cementation depends on the velocity of this reaction and the final conditions of equilibrium of the resulting system. Experiment has shown that the course and the final state of the general reaction written above vary within very wide limits, not only with variations in the nature of the hydrocarbon used but also with the smallest variations in the conditions (temperature, pressure, composition of the steel, etc.) under which this reaction is effected.

If we except the cases in which we work at very low temperatures, the reaction schematically indicated above is in reality considerably more complex, because it consists of the aggregate of many analogous reactions and it is not completely reversible, or, at least, in the system corresponding to the final equilibrium the components indicated in the second member predominate enormously. Since we do not usually work at very low temperatures, because of the consequent slowness of the process, cemented zones of *excessively high* carbon content are almost always obtained.

Moreover, even when starting with a pure, chemically definite hydrocarbon, the reaction which takes place in reality never has the simplicity of that schematically written above; thus, for example, the hydrocarbon $C_{m-x}H_{n-2y}$ indicated in the second member is, in practice, replaced by a mixture of various hydrocarbons. And the complexity of the phenomenon increases enormously when, as happens normally in practice, the gas or the vapor used does not consist of a single, chemically definite hydrocarbon but of a mixture of various hydrocarbons.

All these cause the general physico-chemical study of the processes of cementation with hydrocarbons to present enormous difficulties, and lead to results of great complexity.[1]

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[1] For all these reasons we must consider the assertion of Charpy which I have cited on p. 55 to be without foundation. We must consider it as certain that, *in practice*, hydrocarbons used *alone* as cements cannot furnish "automatically limited" cementations, in the sense in which Charpy uses this expression.

Moreover, the same phenomena make it in practice exceedingly difficult, if not impossible, to conduct a cementation with a cement having hydrocarbons as base, in such a way as to obtain a well-defined result, owing to the complexity of the reactions which take place in the cementation boxes. If we work at very low temperatures in order to avoid cemented zones of high concentration of carbon, the process becomes exceedingly slow.[1] For these reasons the use of volatile hydrocarbons is not advantageous in those most frequent and important cases in which it is desired to obtain cemented zones of a certain depth (for example, more than a millimeter), and where a predetermined, well-defined result must be obtained, or where it is important that the concentration of the carbon should not be too far removed from a certain value and that the distribution of this carbon should be as uniform as possible and show no sudden variations.[2]

On the other hand, none of the disadvantages mentioned above is presented by the cements whose activity is due to carbon monoxide. In fact, the reaction to which the carburizing action of carbon monoxide is due, either when acting alone or in the presence of free carbon on iron at a high temperature, is *exclusively* the following:

$$2CO \rightleftarrows CO_2 + C$$

This reaction is simple, perfectly reversible at the temperatures at which the cementation is effected most rapidly, and leads to equilibrium with great rapidity in the presence of the iron, which is, for this reaction, an efficient catalyzer.

Moreover, the conditions of equilibrium of this reaction are exactly such as permit, when working under the conditions best adapted to obtaining in a given time a cementation of maximum depth, of obtaining practically, in the cemented zones, the concentration and the distribution of the carbon usually desired in the cemented articles.

Finally, the course of this reaction, as to the states of equilibrium to which it can lead, under the most varied conditions of temperature, pressure, composition of the steel, etc., are so well known, from such a great series of experimental and theoretical data, as to make possible an exact preliminary determination of the conditions best adapted to obtaining a certain practical result, and thus render easy a rigorous control of the operation.

Since the specific carburizing action of carbon monoxide constitutes the absolutely essential element of all the more important processes of cementation used industrially, and since the general laws which govern this carburizing reaction are known, it seems well to develop here briefly some considerations which it is absolutely necessary to take into account when it is desired to apply these general laws to practical cases such as present themselves in technology.

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[1] This had already been observed from the time of the first scientific investigations on cementation; for example, by Caron (see p. 6).

[2] We have seen (see p. 106) how even in cementations carried out at a relatively low temperature it is not possible to avoid at least a sudden variation in the concentration of the carbon in the cemented zone.

The reactions concerned in the specific action of carbon monoxide have been the subject of many experimental researches, and the *general* laws which govern their course and the state of equilibrium to which they lead have been enunciated in simple and clear form by Schenck. The theoretical considerations developed by Schenck constitute the necessary foundation for the correct interpretation of these phenomena. For obvious reasons of convenience, we can reproduce these considerations here only in abstract, and I must assume that those who wish to master completely and rigorously the laws which govern the phenomena will study the results of the investigations of Schenck and of his students, or at least as much of them as is reported in Chapters IV and V of his volume on the "Physical Chemistry of the Metals." I therefore limit myself here to making observations on the applicability of Schenck's theories to the practical study of the processes of cementation by carbon monoxide.

First of all, it is necessary to remember that the conclusions of Schenck hold without modification and exactly only in the case in which the various reactions proceed freely until they reach *complete equilibrium*. The course of the reactions which are effected in the system formed of carbon monoxide, carbon dioxide, and iron-carbon mixed crystals hold with exactness only in the case in which the concentration of the carbon is uniform throughout the whole mass of the mixed crystals. But this uniformity can be attained in the time available in practice only when the iron being cemented is subdivided into small masses (wires, granules, filings, etc.), while in the more general practical case of cementation of larger articles, the carburization is limited to the peripheral zone of the pieces and in this zone the concentration of the carbon varies (decreasing) as we pass to the successively deeper layers. It is clear that in this last case we cannot speak of *complete equilibrium*. Also, to the three factors (pressure, temperature and composition of the gaseous mixture) on which in the first case the final result of the cementation depends, are added two others: the velocity with which the gases diffuse into the steel and the velocity with which the carbon diffuses in this steel. Experiment, however, shows that, under the conditions of temperature and of pressure at which the cementation is ordinarily effected, the two new factors act with insufficient intensity to produce a *qualitative* change in the phenomena, and barely sufficient to produce a *quantitative* change in the relation between the maximum concentration of the carbon in the surface layer of the cemented zone and the composition of the gaseous phase.

A proof (among the many which I could cite) of the correctness of these assertions is furnished, for example, by the results of the experiments described on pages 135–136, from which it follows that even when the cementation is limited merely to one zone of the pieces of steel there exists a definite concentration of the mixed crystals, corresponding to that special gaseous mixture which is present, under equal conditions, in equilibrium with the form of free carbon present.

The intervention of the two new factors is, on the other hand, placed in evidence by the fact (see p. 167) that on reducing, by dilution with nitrogen, the partial pressure of the mixture of carbon monoxide and of carbon dioxide acting on the iron, *in the presence of wood charcoal*, all the other conditions being equal (and only for cementations of slight depth), the maximum concentration of the carbon in the cemented zones decreases markedly. In fact, if such variation did not occur in the relation between the velocity of the reactions and the velocity of the diffusion of the carbon and of the gases, no variation whatever could manifest itself in the concentration of the carbon in the mixed crystals, for it is proved[1] that in the diagram of the pressures and compositions of the gaseous phase (at constant temperature) the equilibrium curve corresponding to a given form of free carbon coincides *wholly* (for any pressure whatever of the active gases) with the equilibrium curve corresponding to mixed crystals of a definite concentration.

Similar considerations may be deduced from the fact that Schenck's conclusions hold for reactions which develop in a definite mass of gas kept *entirely* under the conditions (of temperature, of pressure, etc.) considered, and during a time sufficient for the attainment of complete equilibrium, while in the practice of cementation the gaseous mass acts in the form of a *current*, so that at any moment only a portion of the gas used is in a position to react under the normal conditions chosen for the operation. It is evident, therefore, that the velocity of the gaseous current intervenes in practice as another factor modifying the final result of the cementation such as it would be deduced from the laws of chemical statics. This new factor, however, like the two cited before, can give rise to only quantitative and not to qualitative modifications of the results predicted on the basis of the laws of chemical statics. This is because, under the usual conditions of temperatures higher than 800° C. and in the presence of iron acting in this case as an efficient catalyzer, the velocity of the reactions taking place in the gaseous phase is so high that they are practically completed in the interval of time sufficing for the renewal of the mass of gas in the cementation box.[2]

This is also confirmed by the attainment in the cemented zones of a well defined concentration of the carbon, corresponding to the gaseous mixture in equilibrium with the free carbon, and this even in the case in which the gaseous mixture is made to act in successive portions in the form of a current.

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[1] See Schenck, *Chimie physique des métaux*, pp. 199–201.

[2] On the velocity of these reactions see, for example, the investigations of Bell (1869), of Boudouard (1901), of Schenck and Zimmermann (1905), etc., and the recent ones of F. E. Rhead and Richard V. Wheeler (*The Journal of the Chemical Society*, November, 1910, pp. 1140–1153).

Finally, we have seen how in practice it is necessary to also take into account the unavoidable oscillations in the temperature which may manifest themselves during the cementation. In fact, we have already seen how such oscillations, for the reasons already pointed out by Osmond (see p. 31), and by Charpy (see p. 42), and later better developed by Benedicks and by myself and by G. Scavia (see p. 159), may give rise to very great increases in the concentration of carbon in the cemented zones; increases entirely independent of the maximum value which the concentration of the carbon may attain (in the case of complete static equilibrium) under the conditions under which the cementation is effected. This is shown experimentally in a very clear manner by the experiments cited on page 160.

When the observations which I have just set forth are taken into account, it will be easy for every one to find in the theoretical discussions of Schenck a rigorous scientific explanation of the facts which I have noted and a simple explanation of the special behavior of carbon monoxide in the cementation process.

In connection with the theoretical considerations developed by Schenck, I think it well to make still some observations on another point which may, in some special cases, assume marked practical importance.

In the diagram of complete equilibrium traced by Schenck for temperatures below 700° C., at which the iron-carbon mixed crystals are not formed, there appear also equilibrium curves corresponding to the reactions in which oxides of iron and metallic iron (two by two) act with the gaseous phase. At temperatures higher than 700° C., that is, temperatures at which iron-carbon mixed crystals are formed and which alone are of real practical interest in the study of cementation, Schenck observes that those curves of monovariant equilibrium cease to be of interest because, from 750° C. up, the reaction pressures corresponding to them exceed one atmosphere.

This is certainly correct for the cases occurring most frequently in practice, and, in fact, in the general study of the cementation of ordinary steels with carbon monoxide it is never necessary to consider the case of the formation of an oxide of iron. But there are two cases which I think it well to specially point out here, in which these equilibrium curves present great interest. The first is that of cementation carried out with carbon monoxide (pure or in the presence of free carbon) under pressures higher than atmospheric. We have seen, in fact, that recent experiments have confirmed the great importance which the exact knowledge of the position of these curves has in this case in the determination of the lower limit of temperatures which can be practically used. The second case is that which we have seen presents itself (see p. 156) in the cementation of special steels, when the oxidation curve of the steel subjected to cementation with carbon monoxide is displaced, with respect to that corresponding to pure iron, so far toward the mer the reaction pressure (corresponding, in this case, to its intersection with the curves of cementation) falls until it re-enters the field of the pressures used for cementation.

This shows itself in industrial practice by the phenomena which every one may have observed and is seen also from the experiments of Charpy (see p. 112) on the cementation of chromium, of manganese, and of chromium and chromium-nickel steels, with carbon monoxide.

I have already pointed out (see p. 149) that the experiments of Charpy just cited were carried out from a practical standpoint, and without taking into account in any way the studies of Schenck. If these studies are taken into account, we can reach a clear and complete interpretation of these phenomena. But from those experiments, besides the pure and simple determination of the fact that the presence of the chromium in the steel lowers (for equal temperatures) the point of intersection of the curves of cementation and of oxidation of the metal, so as to make it correspond to a pressure lower than the atmospheric pressure, there follows another interesting datum, consisting in the empirical observation of Charpy that the oxidation of the metal is limited to a very thin surface layer when the cementation of steels of medium or low chromium content is carried out with carbon monoxide at about 1000° C. This fact, the practical importance of which is evident, is easily explained when we consider that the minimum limiting pressure of oxidation increases with rise in the temperature, so that at 1000° C. the cementation can, for certain steels, proceed under ordinary pressure without being accompanied by oxidation, and only during the initial heating and the cooling which follows the cementation does the system traverse the interval of temperature within which the cementation is accompanied by oxidation. It is clear that under these conditions the oxidation can be only superficial.

From these observations is seen the importance of determining the relation of temperature to the pressures of monovariant equilibrium for the special steels which it is desired to subject to cementation by the specific action of carbon monoxide. The experiments of Schenck and Semiller on the alloys of iron and manganese already furnish precise data on the lowering which the equilibrium point undergoes with increase in the manganese content, and show that this lowering is great for even relatively low manganese contents. It is sufficient to prove it to report three data relative to a temperature of about 950° C.—one of the most frequently used in cementation.

Manganese content	Temperature	Pressure
0.00 percent.	950° C.	Much higher than 2 atmospheres
0.95 percent.	950° C.	802 mm.
4.01 percent.	965° C.	46 mm.[1]
6.38 percent.	956° C.	20 mm.

Analogous variations, though not so great, are observed for many of the alloys of iron most frequently used in practice. This is seen in chromium, and chromium-nickel steels, etc., from the results of my and Doctor Carnevali's experiments which I have cited and examined in detail, also from the point of view of their theoretical interpretation, in the preceding chapter (see p. 146).

The numerous experimental data set forth in the preceding chapter confirm fully these conclusions, showing the ease and the certainty with which the rational use of carbon monoxide in the cementation of steel permits of obtaining cemented zones in which the maximum *concentration* of the carbon does not exceed a definite and pre-established value and varies from one layer to the other of these cemented zones as desired. No other carburizing substance permits of such control. The variety of the types of *distribution* of the carbon in the cemented zones which can be thus obtained permits of obtaining with certainty in any practical case the product which is best suited to its purposes.

It can, therefore, be asserted that the cements with carbon monoxide as base, and, more especially, those whose action may be regulated,[1] are the most perfect cements. They offer the greatest guarantees of well-defined and uniform quality of the product, together with the amplest opportunity of adapting the quality of the product to the conditions which it must satisfy.

Before closing this chapter, I think it well still to review briefly, on the basis of the most recent and reliable experimental data, the results obtained by various experimenters on some other problems in the processes of cementation. I shall omit various questions of secondary practical interest, such, for example, as that of a "reciprocal" phenomenon of the cementation proper, consisting in diffusion of the iron into the carbon (see Colson, p. 25, and Osmond, p. 28), or that, also treated by Osmond (see p. 28), of the eventual necessity that the diamond undergo a "molecular transformation" to be able to cement iron. Thus, too, I shall not deal with questions on which experiment has yet furnished only scarce and uncertain data; such, for example, as the question of electrical cementation (see p. 28).

A series of experimental data of great practical interest is that which concerns the relations between the temperature at which a given process of cementation is effected and the quality of the product obtained. In all this group the only reliable data are those furnished by the more recent researches, the only ones in which the measurement of the temperatures was made with precision.[2]

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[1] This does not happen, for example, in the cements in which the carbon monoxide is a secondary product of the dissociation of a carbonate added to the other components of a solid cement.

[2] See, for example, the observations which I made in connection with the investigations of Mannesmann (see p. 17). Also in the recent investigations of Ledebur (see p. 60) the measurement of the temperature was made exclusively by means of Seger cones, which, as is well known, permit of only a very rough approximation.

A first fact, enunciated successively by many experimenters (see Mannesmann, p. 16, Guillet, p. 47; and very recently Bruch, p. 66) and known by all practitioners from the earliest times cementations were effected, is the great increase which the velocity of cementation undergoes with increase in the temperature, meaning by "velocity" of cementation the "depth" attained by the cemented layer in the unit of time.[1] As to the importance of this increase, that follows from the diagram of Fig. 19 on page 71.[2]

The effects which variations in the temperature produce on the *concentration* of the carbon in the cemented zones have also been the subject of numerous observations. We may recall as examples the investigations of Osmond cited on page 28; those of Arnold (see p. 32), and many others. But in this field also, only the most recent investigations have given precise and concordant results, and this because, contrary to the earlier researches, the new investigations were carried out with cements of simple and well-defined chemical nature, working at constant and exactly measured temperatures, and the results controlled by exact gravimetric carbon determinations made on various successive layers of the cemented zones.

These recent experiments, carried out with more exact methods, have furnished new, precise proof of the practical importance of the relations between the temperature of the cementation and the concentration of the carbon in the cemented zones which are obtained by means of the action of carbon monoxide. These relations are profoundly different from, and in many cases directly opposite to, those which hold for the other cements.

Finally, the study of the relation between the temperature at which the cementation is effected and the result of the operation gives rise to a third question, *viz.*, what is the lowest temperature at which the cementation can be effected.

Many experiments, such, for example, as those of Mannesmann (see p. 17), of Charpy (p. 45), of Bruch (p. 66), etc., would prove that even at relatively low temperatures, below 700° C. and even as low as 500° C., certain cements, and especially carbon monoxide, produce the diffusion of appreciable quantities of carbon into the mass of the steel. But more recent experiments, carried out with more precise means of observation (see p. 88), prove, for example, that with ordinary soft carbon steels a true cementation proper, meaning the formation of a zone of steel of higher carbon content than that of the rest of the metallic mass and endowed with the structure of a true steel proper having this greater carbon content, can be obtained only at temperatures above 780° C., and that, in general, for all steels the cementation assumes its regular and normal course only at temperatures at which the iron assumes the form of γ-iron. This explains the fact that the special steels, for which the transformation points are markedly low as compared with ordinary steel of equal carbon content, can be cemented at lower temperatures than the ordinary, equally carburized steels.

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[1] I have already explained in the footnote on p. 174 the cause of an experimental result apparently contrary to this rule, obtained by Charpy.

[2] The analogous diagrams of Mannesmann do not furnish reliable data on account of the inexactness of his temperature determinations.

This would explain also the assertion of Guillet (see p. 54) that (γ-iron) polyhedral steels can undergo a true process of cementation (or "diffusion of structural carbon") even at ordinary temperature. The same considerations would explain the influence of the initial carbon content in the steel on the minimum temperature of cementation.[1]

Another group of investigations of great practical importance is the influence of the nature of the cement on the course of the cementation, on the velocity of the penetration of the carbon, on the maximum concentration and on the distribution of the carbon in the cemented zones, etc. Recent experiments, carried out[2] with simple and chemically definite cements so as to isolate the individual processes of carburization, have established quite sure and precise data on the relations which exist between the nature of the cement, the course of the cementation, and the results which it is desired to obtain.

The observation of Caron (see p. 6) of a relation existing between the "decomposability" of the cement and the concentration of the carbon in the cemented zone, and that of Mannesmann (see p. 21), that the "degree of carburization" is proportional to the difference in the "affinity which the carbon has for the iron and for the substances with which it is combined in the cement,"[3] are confirmed in more precise form by the more recent experiments; for example, by those on the carburizing action of carbon monoxide, pure and mixed with volatile hydrocarbons. On the contrary, the assertion of Guillet (see p. 48) that the velocity of cementation varies at first with the nature of the cement but later becomes equal for all the cements when the operation is prolonged beyond a certain time (in general, eight hours at 1000° C.) is not confirmed by the recent experiments with cements having carbon monoxide as base. It is therefore quite probable that the equalization of action observed by Guillet is due to the "exhaustion" of the cements; while it follows with certainty that the velocity of the cementation, even for very long operations, varies with variations in the nature of the cement and is a maximum for a current of carbon monoxide acting in the presence of free carbon.

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[1] We must consider as based on inexact experimental data the observations of Arnold and MacWilliam (see p. 37) on the sudden increase in the minimum temperature of cementation; an increase which, as we have seen, manifests itself when the carbon content of the steel subjected to cementation reaches the value of 0.9 % and which the authors explain by the hypothesis (now proved to be inexact) of the existence, together with the cementite, of a second carbide of iron corresponding to the formula $Fe_{24}C$.

[2] Even in very recent times various experimenters used complicated cements, of undefined chemical nature, in investigations of a scientific character. See, for examples of this, the investigations of Scott (p. 68), of Bannister and Lambert (p. 69), and others which I have cited in the preceding chapters.

[3] The further conclusion drawn by Mannesmann, that the "highest" cementation must be obtained with free carbon, is not justified by the more recent investigations.

Only recently has attention been given to the relations which exist between the nature of the cement and the distribution of the carbon in the cemented zones, and an exact account taken of this distribution. Among the few and incomplete references to this made by the earlier investigators, the most precise are those of Mannesmann (see p. 15) who observed in the very intensely cemented zones sudden variations in the concentration of the carbon, corresponding to the surfaces of passage from the layer transformed into cast iron to that in the state of steel or of iron.[1] Arnold (see p. 33) gives a few "concentration-depth" diagrams, but he limits himself to deducing that the concentration of the carbon in the cemented zones decreases with increase in the depth of the layers analyzed, calling attention, also, to the existence of "three distinct strata" in the cemented zones. The micrographs reproduced by Arnold, however, show that the three strata observed by him do not coincide with the three characteristic layers (hyper-eutectic, eutectic and hypo-eutectic) which I have studied in the preceding chapter, where I indicated the causes of their formation.

Moreover, even in many of the more recent experimental researches, the gravimetric determinations of the carbon are limited to one layer (see, for example, the investigations of Guillet, in which the first surface layer, 1/4 mm. thick, is analyzed) or to two layers (see Charpy, p. 112).

Quite discordant also are the conclusions reached by various experimenters in regard to the influence which the initial content of carbon in the material subjected to cementation exercises on the course of the cementation. A case of such discordance was the polemic which developed between Guillet and Ledebur with regard to the theory of cementation (see especially pp. 59–63). After it was proved that in practice the specific carburizing action of the gases always has a preponderant importance as compared with the action exercised directly by the carbon "by contact," the complicated arguments of Mannesmann (see p. 22) and others as to why the more highly carburized steels are cemented more rapidly than steels with a lower carbon content lose their point and purpose. This fact, now confirmed by precise experiments, constitutes a further proof of the slightness of the direct carburizing action of carbon as compared with that exercised by the carburizing gases.

Similar discordant results were obtained by various experimenters in investigations on the maximum concentration of the carbon in the steel which can be attained when working under definite conditions. Such are the results of the investigations of Mannesmann (see p. 15), of Osmond (see p. 28), of Roberts-Austen (p. 29) and of Saniter (p. 31).

These discordances have been explained, although in a not entirely exact manner, by Osmond (p. 31), and later by Charpy (p. 42) and by Benedicks (p. 159). The latter showed, with very simple reasoning from his experiments, the impossibility of attaining by means of cementation a definite maximum concentration of the carbon, corresponding to saturation of the iron, except by keeping the temperature rigorously constant during the whole of the cementation. Still more recent considerations and experiments (see pp. 160–167) have furnished direct proof and a clear theoretical explanation of the effects which even slight oscillations in the temperature produce on the apparent limit of saturation of the iron by the carbon in cementation experiments.

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[1] See a more precise study of this phenomenon by Giolitti, Carnevali and Tavanti: *Ricerche sulla fabbricazione della ghisa malleabile*, Nota III (*Rassegna Mineraria*, 1910).

As to the cementation of the special steels, there is not much to add to what has been said in the preceding chapters. Caron (see p. 9) made the first investigations on the effects in cementation of foreign substances (such as manganese, silicon, etc.) alloyed with the iron. Guillet (see p. 52) studied essentially practical problems, such as the velocity of the cementation in various special steels, and the obtaining of zones of martensitic or polyhedral steel by cementing certain pearlitic steels.

The investigations of Charpy on the cementation of the special steels with carbon monoxide have been already noticed in the present chapter (see p. 191). We have also already reported the more precise data obtained in recent investigations on the distribution of the carbon in the cemented zones, and the exact definition of the conditions under which cements with carbon monoxide as base can be advantageously employed for the cementation of the various types of special steels (see p. 145).

A last group of investigations of great practical importance are the studies on the diffusion of the other elements than carbon into iron at a high temperature but still in the solid state. The experimental data published up to the present on this subject are few and not wholly reliable. We may mention here the experiments of Boussingault on the variations in the concentration of the sulphur contained in iron during cementation (see p. 23); those of Campbell and of Arnold and MacWilliam (see p. 34) on the diffusion of the sulphide and oxysulphide of iron into iron, and those of Arnold and MacWilliam on the diffusion of various metals into solid iron.

In connection with these last experiments, I must point out that recent investigations (to which we will refer in the second part of this book) do not confirm the division made by Arnold and MacWilliam (see p. 35) of the various elements into two classes, the first of which includes the elements capable of diffusing or "migrating" into the mass of the solid iron, while the elements belonging to the second class lack this power. The experiments to which I have just referred prove that the various elements classified by Arnold and MacWilliam in the second class can diffuse into solid iron, under suitable thermal treatment.

PART SECOND

STRIAL APPLICATIONS OF THE PROCESS OF CEMENTATION

INTRODUCTION

In the first part of this volume, we have tried to bring together all the data acquired up to the present on the process of cementation; it is only on the basis of these data that practical rules for operating processes of cementation can be derived.

In the second part of this volume we propose to consider the material means which modern technology uses for the practical application of these rules.

Since there are two essential objects for which the process of cementation is applied, we will therefore devote two separate chapters to the applications of cementation, on the one hand to the total transformation of wrought irons and soft steels into hard steels, and on the other to the superficial carburization of machine parts. In the second chapter I shall also refer briefly to some other processes which, while they cannot strictly be classified in either of the two preceding groups, present many characteristics in common with the processes of the second group, both as to the principles on which they are based and the objects at which they aim.

Although we are considering the subject of cementation, still it will be necessary also to deal briefly with the various complementary treatments of the cemented materials (such as tempering, annealing, etc.), especially since the effects of these treatments are closely connected with those of the cementation, and above all since they influence to a marked degree the results of the various methods used for the technical control of the cemented products.

We add also some data on the measurement of high temperatures, assuming a general knowledge of the same and limiting ourselves to the arrangements more especially adapted to the control of the temperatures in cementation.

Finally, I will add some data relative to the more important patents which deal with processes of cementation.

CHAPTER I

TOTAL CEMENTATION OF WROUGHT IRON AND SOFT STEEL

I have already pointed out on p. 4 that the cementation of steel began to assume a large industrial development in the first years of the seventeenth century, when from a simple process for the superficial hardening of objects of soft iron it became a true process for the manufacture of steel; when, that is, it was applied to the total transformation of pieces of soft iron or steel into hard steel intended for further heat treatment.

This manufacture of cement steel received a strong impetus in 1740 by the invention, by Benjamin Huntsman, of the process of crucible fusion of steel; so that, toward the end of the eighteenth century, the industry of the manufacture of cement steel destined for crucible fusion attained a great development.

Notwithstanding the subsequent decline of this industry in the nineteenth century, due to the marvellous development of other modern processes for the manufacture of steel, the technical importance of the processes of cementation, instead of diminishing, kept on rapidly increasing, for a reason inverse, so to speak, to that which had given it its great impetus at the beginning of the seventeenth century. In fact, while formerly the industrial development of these processes was due essentially to their application to the total transformation of soft iron or steel into hard steel, the further development of these same processes in the second half of the nineteenth century and in the first years of the twentieth is, on the contrary, due to their application to the superficial carburization of machine parts. This is explained by the recent great advances in the technology of mechanical construction.

The present causes of the slight importance of the older, original processes, at least as regards the quantity of the products manufactured by them, are above all of an economic nature, and are essentially the high price of the steel obtained by cementation as compared with the price of steels of corresponding quality obtained directly by other processes, such as, for example, the electric furnace. But besides these causes of an economic nature, others of a technical character serve to diminish their industrial importance. First among these is the increasing application of the special steels, whose properties render them for many uses far superior to the best carbon steels obtained by melting the purest cement steel in crucibles. The technology of the direct manufacture of the special steels by means of the so-called processes of "metallic cementation" is in its infancy, and has not yet given really practical results.

From what has been just said, it is seen that any one desiring to study the part which is still played to-day in siderurgy by the manufacture of cement steel intended for fusion should attempt to seek the reasons of its survival rather than of its decline.

The industry is certainly gaining ground, for, according to the manufacturers of crucible-fused steel, the high-carbon product obtained by fusing wrought iron *first carburized by cementation* is far superior to that which is obtained by carburizing the steel during the fusion.

Still further, the product which is obtained by cementing best Bessemer or Siemens-Martin soft steels and *then* melting them in a crucible is considerably inferior in quality to that obtained by using as raw material good wrought iron and treating it, in other respects, in an identical manner.

No precise comparisons have been made of the qualities of the products of identical composition obtained by the various processes just mentioned, and it does not seem, in the present state of our knowledge, that a complete explanation can be given for the differences noted by practitioners in the qualities of these products. Some regard as an explanation the fact that the cementation of wrought irons permits of obtaining perfectly sound steels of very low manganese and silicon content, while it would not be possible with the other processes to reduce the percentages of these two elements to such low values without the steel becoming oxidized and brittle, as well when hot as when cold. On the other hand, it does not seem that there can be any reasonable doubt as to the reality and the constancy of these differences in quality, for there is no doubt that manufacturers would not hesitate to substitute the less expensive soft steel for wrought iron, if their experience had not proved the marked inferiority of the products obtained with soft steel.

I believe, therefore, that steels of high carbon content obtained by melting cemented best wrought iron in a crucible are uniformly of better quality than products of the same composition obtained either by carburizing fused soft steel or by fusing cemented soft steel. It is to this difference in quality that is due the survival and recent rejuvenation of the cementation industry for manufacturing high-carbon steels of superior quality.

The most important center of this industry to-day is Sheffield. But it is also practised in various other places, both in England and in France, the United States of America, Germany, Austria, Sweden, etc. In Italy, where it flourished in the seventeenth century (see p. iv), it still survives in Lombardy.

Using the expression in its widest sense, we must include in the processes of the manufacture of cement steel all those which are based on the carburization of the iron or steel by keeping it in contact with carburizing materials at a temperature not high enough to completely melt it.

These processes may be divided into two groups; to the first group belong those in which the operation of the carburization is effected simultaneously with that of the reduction of the iron ore, or at least directly on the iron such as it results from the reduction of the ore; to the second group, on the contrary, belong the processes in which there is subjected to carburization iron or steel which has already undergone a series of treatments for freeing it of the greater part of the foreign substances (scoriæ, etc.) and for fashioning it into definite sizes and shapes ("bars").

The processes of the first group have now only a historical interest; I limit myself, therefore, to referring briefly to some of them. Two English patents, granted in 1854 and 1856 to Samuel Lucas and to W. E. Newton, respectively, describe two processes, very similar to each other, consisting in heating for a long time in closed refractory vessels small fragments of iron ore mixed with an *excess* of pulverulent carbon (wood charcoal, animal charcoal, etc.); the product obtained ("sponge") must be crucible-fused. These processes, which various later experimenters attempted in vain to apply, present (besides many other defects) the serious disadvantage of never furnishing results which are uniform or which can be predicted on the basis of the composition and the proportions of the raw materials used.

Another process belonging to this same group is the Chenot process. This process, which on its appearance in 1857 gave rise to great hopes of success, presents over its predecessors the advantage that the carburization, while effected on the metallic sponge resulting directly from the reduction of the iron ore, is carried out separately from the reduction of the ore; this makes it possible to determine with some approximation the carbon in the final product. In the Chenot process the iron sponge was intimately mixed with powdered wood charcoal impregnated with tar or with fatty substances, and then heated in closed vessels; the cemented sponge was compressed into cakes and then fused in a crucible. According to Percy (treatise on Iron and Steel) the price of Chenot steel manufactured at Clichy was 1097 francs ($210) per ton.

The most serious disadvantage of the Chenot process lies, according to Percy, in the large volume occupied by the cemented sponge, even though strongly compressed; this does not permit of a good utilization of the space disposable in the crucibles in which this sponge must be melted, causing a very high cost for fusion.

Neither the Chenot process nor the other analogous ones which have followed it have justified the great hopes raised by their appearance, and today they may be considered as being abandoned.

The only processes of cementation at present in use for the manufacture of steels destined to undergo further working are those which we may call "processes of cementation of iron in bars." The importance and the diffusion of these processes are not great at present, not more than at or about the middle of the last century. Several inventions have been based on some supposed new process of cementation, but all such have quietly disappeared. I shall recall, as a single example, the "Bates process."

Francis Gordon Bates, of Philadelphia, obtained in the principal countries a series of patents between 1890 and 1893. According to the description of one of his first patents (German patent, Kl. 18, No. 57,729, May 20th, 1890), his process consists essentially in cementing iron by means of a mixture composed of 80 to 100 parts of carbon, 5 to 10 parts of cryolite, 10 to 20 parts of spent lime and 5 to 10 parts of rosin or soda. In another patent (German pat., Kl. 40, No. 63,404, of November 3rd, 1891), Bates describes a furnace with three hearths, designed for the carrying out of his process. In a third patent (German pat., Kl. 18, No. 83,093, of February 23rd, 1893), the inventor claims a further improvement of his cementation powder, consisting in adding to the ingredients already indicated in the preceding patents nickel oxide; according to Bates, this oxide is reduced during the cementation and the nickel alloys directly with the iron subjected to the treatment.

The Bates process was given wide publicity, and various technical reviews, especially English, dealt with it repeatedly, announcing it as destined to bring about a revolution in the manufacture of steels of superior quality. *Stahl und Eisen*, in March, 1893,[1] commenting on an article on the Bates process in the English journal *Iron* in which it was asserted that the new process had reduced to 7 pounds sterling per ton the price of steels identical in quality with so-called Mushet-steel, then sold in England at 140 pounds sterling per ton, says that if this process is merely an application of the patents obtained by Bates the manufacturers of fused steels of superior quality need in no wise fear the announced "revolution," and concludes by advising the author of the *Iron* article to test the steels manufactured in German steel works, either in convertors or in the Martin furnace, in order to convince himself that the Bates process is superfluous.

The making of cement-steel in bars is limited at present to the production of very pure steels of high carbon content and of superior quality for springs, files, etc.

The material which furnishes the best steel by cementation is wrought iron of the purest quality. This is partly explained by the purity of the wrought iron, which is in general superior to that of the fused soft steels, at least as regards the substances forming an integral part of the metal, such as substances in the state of solid solution (manganese, silicon, sulphur, etc.). The harmful influence of slag, always much more abundant in the wrought iron, does not make itself markedly felt in the cemented products, from which it is in great part eliminated by the subsequent treatments to which the cemented bars are always subjected, especially so when such treatments include crucible-fusion.

For many years the cement-steel manufacturers of Sheffield, the principal center of this industry, used almost exclusively as raw material the best qualities of iron imported from Sweden. Later, they also used materials

[1] Vol. XIII, pp. 217-218.

from other sources, and especially Russian wrought irons; but they always held and hold now that the use of fused soft steel in place of wrought iron furnishes a product far inferior in quality.

Another fact which almost all manufacturers of cement steel consider as certain, and on which is based one of the rules constantly followed by them, is the superiority of the product obtained by cementing *hammered* iron bars as compared with that furnished, under the same conditions, by *rolled* bars. Moreover in the industry with which we are now dealing, the greater part of the manufacturers strictly follow tradition and, in the absence of precise technical data, prefer to follow with minute accuracy the rules which the experience of centuries has shown to furnish good results, rather than to try the slightest innovations. Thus the various manufacturers have their preferences for irons of certain definite brands; but they do not take much care to find out just what the material furnished them under the preferred brand really is.

For this reason it seems to me superfluous to give detailed information as to the qualities of iron most widely used for the manufacture of cement steels. The number of the "brands" of cement iron which have stood and now stand in high repute is not small; such are the "Hoop L," "Double bullet," "CCND," "Little S," "OO" "W.W" brands, etc.

As an example we may cite the analysis of a Swedish iron, capable of furnishing, by cementation, a steel of the best quality:

Carbon	0.050 percent.
Silicon	0.045 percent.
Manganese	0.025 percent.
Sulphur	0.007 percent.
Phosphorus	0.010 percent.

As is seen, this is a material of high purity.

Thus, too, the iron obtained from the celebrated Denmark ores and placed on the market under the brand "Little S" is of marked purity, although somewhat rich in manganese; its composition, according to the analyses of Arnold, is as follows:

Carbon	0.050 percent.
Silicon	0.037 percent.
Sulphur	0.006 percent.
Phosphorus	0.012 percent.
Manganese	0.108 percent.
Copper	traces.
Arsenic	0.007 percent.

In many places (for example, in Westphalia, Germany, and in various English iron centers, etc.,) puddled iron is also used as raw material for the manufacture of cement steel. I cite, as an example, the composition of an English puddling furnace wrought iron:

Carbon	0.16 per cent.
Silicon	0.00 per cent.
Manganese	0.09 per cent.
Phosphorus	0.09 per cent.
Sulphur	not determined.

As regards the carburizing substance, or "cement," many mixtures have been proposed with the object of accelerating the process, and of these I have already mentioned the mixture proposed by Bates.[1] But the number and the complexity of the carburizing materials proposed for total cementation remain far behind those reached by the "cementation powders" proposed for superficial cementation. The greater part of the manufacturers of cement steel have not abandoned the use of simple powdered wood charcoal, or have returned to it after unfortunate attempts to make use of more complex mixtures. This is probably due to the fact that the foreign substances in these mixtures, passing from the cement into the steel, impair its properties to a much greater degree in the processes of total cementation than in those of superficial cementation. This is because the quantity of the harmful substances which the steel absorbs in the processes of total cementation, in which the operation is protracted for a period ten to twenty times longer, is, all other conditions being equal, much greater than that which can diffuse into the metal in the processes of superficial cementation, and also because in the former processes much greater stress is laid on the high quality of the product. It follows that the foreign substances in the cementation powders used in case-hardening machine parts serve merely to give the manufacturer the illusion of employing an extraordinarily "perfected" agent. They cannot be tolerated in a cement intended to produce deep cementations, for in the latter case their harmful effects on the quality of the product make themselves felt to such a degree as to render impossible any doubt of the harm done.

The most "innocuous" cementation mixtures are those obtained by adding to the wood charcoal some proportion of alkalis or alkali carbonates or carbonates of the alkaline earth metals or animal charcoal, or by impregnating the wood charcoal with aqueous solutions of alkali carbonates, sodium chloride, etc. But among all the cements at present in use, the "surest," and not less efficient than many other more complex ones, is simple wood charcoal, and it is also the most widely used.

As to the quality of the wood charcoal best adapted to serve as cement, it seems certain that the cementation takes place more rapidly with charcoals obtained from compact woods (oak, walnut, chestnut, etc.) than with those obtained from lighter woods (like the poplar, pine, larch, etc.), but the latter are also often used on account of their lower cost.

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[1] Among the substances which have been proposed for total cementation, we may mention the cyanides, the ferrocyanides, borax, alum, vinegar, fats, blood, sugar, horn parings, marine algæ, etc., etc.

The wood charcoal designed to be used as cement is usually subjected to a simple crushing. Of the crushed charcoal, that portion is usually employed which passes through a sieve with square meshes 1 to 2 cm. on a side, and held by a sieve with about 4 meshes per sq. cm.

Experiment shows with certainty that carbon already used for cementing iron loses much of its efficacy. The probable causes of this phenomenon have been the subject of long discussions, especially between Margueritte and Caron, and later between Guillet and Ledebur. The supporters of the hypothesis of the preponderant action of gases in cementation attributed the "exhaustion" of the cements to the gradual elimination by the prolonged heating of the gases occluded in them. That the phenomenon really depends on this is proved by the fact (see p. 135) that the exhaustion does not occur in the slightest degree when care is taken to maintain in the cementation chambers an atmosphere of the gas most active as cement—carbon monoxide. I would add, however, without entering into details (this being a procedure whose technical application on a large scale is still being studied) that the use of "mixed cements" based on the specific action of carbon monoxide has given results beyond all expectations, even in the manufacture of fused steels, totally eliminating the phenomenon of "exhaustion." This confirms fully the hypothesis to which I have referred above.

In ordinary practice the effects of the exhaustion of the cement are remedied by using in each operation only a part of the carbon already used in the preceding operation, and completing the charge with carbon which has not yet been used. Usually, the cement is prepared by mixing one part (and sometimes as much as two parts) of the carbon already used with two parts of new carbon. It is said that expert operators can distinguish by the simple feel carbon already used from that which is new, and this by the fact that the particles of the former are more compact and heavier than those of the latter.

In many cases the carbon already used is subjected, before being used again, to washing, followed by drying, which removes from it the excess of ashes resulting from the combustion of part of the carbon in the preceding cementation.

The furnaces for the total cementation of iron which are still used to-day do not differ much, in their essential parts, from those used two centuries or so ago, when Réaumur published his classical researches on cementation. The slight importance of the changes introduced in more recent times is seen clearly from a comparison of the drawings of the furnaces described by Réaumur and those used a little later in England (see p. ix), with those of the more modern furnaces reproduced herewith.

Figs. 73 and 74 represent sections of a type of cementation furnace widely used to-day. The structure of the furnace is very simple. The two boxes *A*, *A*, designed to contain the bars of iron and the cement,[1] are made of refractory bricks and are placed on the rectangular base of an arched chamber, also of refractory bricks, with their long sides parallel to the long sides of the chamber; the free space at the bottom of the chamber is a hearth,

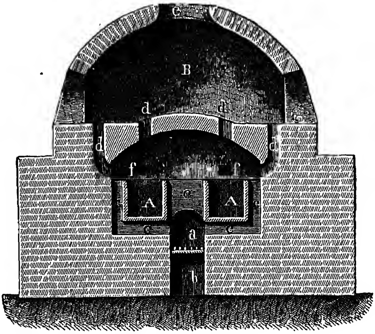

FIG. 73.—(*Ledebur.*)

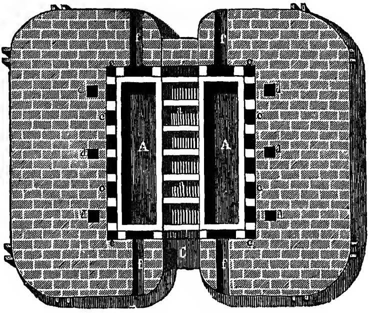

FIG. 74.—(*Ledebur.*)

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[1] Cementation furnaces with three boxes have also been constructed, but they have not given good results because they did not permit of obtaining a sufficiently uniform heating of the boxes.

as long as the boxes and furnished at the two ends with two feeding doors. The grate is lower than the bottom of the boxes. The products of the combustion circulate uniformly around the two boxes and in the space left free between them, through a series of channels formed of refractory bricks, the dimensions and the arrangement of which (as is seen with special clearness in Fig. 74) are so planned as to obtain good uniform heating of the two boxes. Complete uniformity of temperature of the boxes is obtained better, during the heating, by partially closing the mouth of the flues corresponding to the parts of the boxes in which by chance an excessive rise in temperature is observed.

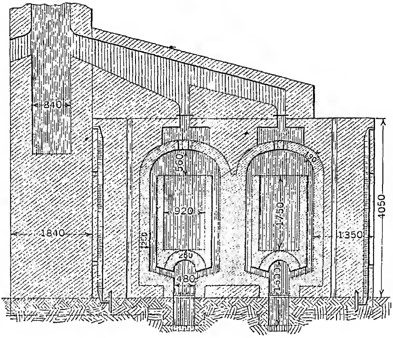

FIG. 75.

The hot gases issue from the chamber through a series of small openings made on two sides of the arch and at the base of it, and from here, through short passages, they pass into a conical chamber of bricks, which covers the whole furnace and is open only at the top. In the two minor walls of the refractory chamber are made two openings which permit of the entrance of workmen into it during the charging of the furnace. Before beginning the heating, these openings are walled up with refractory bricks.

The usual dimensions of the boxes are from 2.50 m. to 4.50 m. in length by 80 cm. to 1 m. in height and in width. Boxes of these dimensions can hold from 6 to 12 tons of iron, together with the necessary quantity of cement.

The outside walls of the boxes are always pierced with one or more holes through which are passed iron bars ("spies") which remain partially immersed in the cement. The examination of these bars, removed from the boxes from time to time, furnishes useful indications as to the course of the cementation. Figs. 75 and 76 reproduce two sections of a furnace constructed on principles identical with the preceding but differing from it in several structural elements, especially in the construction of the refractory chamber containing the two boxes. The characteristics of the construction of this furnace follow clearly from the two figures herewith reproduced.[1]

Other similar types of cementation furnaces are also constructed, in which, however, every box is heated by a separate hearth, so that the various boxes can be kept at different temperatures.

The great advantages of gas fuel, both as to economy in fuel and greater ease and perfection with which the heating can be regulated and made uniform, explains the present tendency to substitute for the old cementation furnaces, heated directly with solid fuel, other furnaces heated by producer gas.

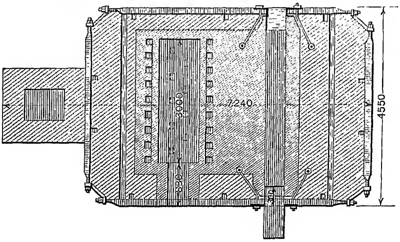

FIG. 76.

As an example, we may show here a modern type of cementation furnace heated by producer gas, and used both for total cementation and for superficial cementation (case hardening).

It is represented, in longitudinal and transverse section, in the two figures, 77 and 78.[2] The gas, produced by the producer A, reaches the furnace through the channel C and is burned in D by a jet of air under pressure; the flame, after having passed over the cover and the sides of the cementation chamber until it reaches the front end of the furnace, returns to its rear end through the two channels F, made, under the box, in the mass of refractory bricks constituting the box itself, and passes then from the conduits F to the channel G and from this to the chimney. The refractory system constituting the box and the two channels for the return of the flames F is placed on a car, so that, the operation being finished and the door of the furnace opened, all that is necessary is to draw out the car and quickly substitute for it another similar one, into whose refractory box the bars of iron and the cement have already been loaded. In this way the process takes place much more rapidly than with the other furnaces with fixed boxes, for the operations of charging and emptying the boxes are carried on outside of the furnace, and it is not necessary to wait for the latter to cool. It is easy to understand how this arrangement has the advantages of greater rapidity of the operations, of greater productive capacity, and of great economy in fuel.

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[1] The four figures (73–76) are taken from Ledebur's *Handbuch der Eisenhüttenkunde.*

[2] This furnace is described by Engineer C. W. Bildt; *Jernkontorets Annaler,* 1901, abstracted by *Stahl und Eisen,* 1902, I, pp. 438–440.

I do not think that experimental data on the working of this furnace have been published, and I have never had opportunity to study it in operation. However, judging it *a priori* on the basis of furnaces similarly constructed, I would consider that its fundamental defect consists in the way in which the channels *F* are connected with the channel *G*. In fact, in the furnaces of this kind which I have had occasion to use, I have always observed that after prolonged operation, which wears out the movable ends of the canals and makes them irregular, it was not possible to obtain a sufficiently tight connection between the fixed channel *G* and that on the car *F*, so that sometimes a considerable part of the gases, instead of following the longer course *DBFG*, followed the direct way *DG* to the chimney. The immediate consequence of this is a large difference in temperature between the two ends of the box, which is more highly heated toward *D* than toward the door of the furnace.

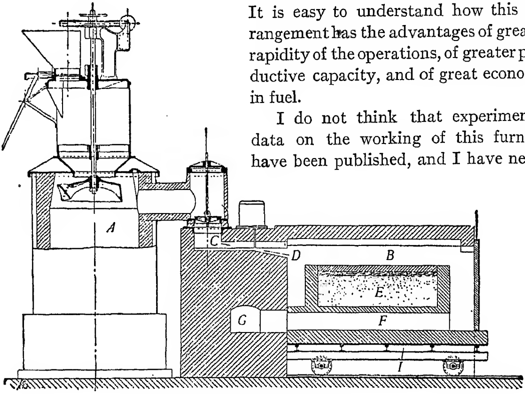

FIG. 77.

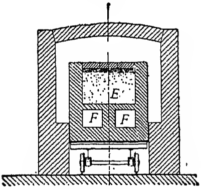

FIG. 78.

Whatever may be the type of the furnace used, the charging of the cementation boxes, when solid cements are employed, is done as follows: On the bottom of the refractory box is placed a layer of fine refractory earth, a couple of centimeters thick, intended to fill the cracks which may eventually be formed during the heating of the furnace, so as to prevent oxidizing gases from penetrating into the cementation boxes and impeding the carburization of the iron. Above the refractory earth is placed a layer of carbon in coarse powder and fragments (or of any other solid cement), 5 to 8 cm. thick, on which is placed a first layer of the iron objects to be cemented. The shape most commonly adopted for these is that of flat bars 10 to 20 mm. thick by 50 to 100 mm. wide; the bars must be about 10–20 cm. shorter than the cementation boxes in order that between their ends and the walls of the boxes a sufficient quantity of carbon may stay, even when the bars have expanded as a result of the high temperature of the furnace. The bars of iron must be placed flat and carefully surrounded by the cement; they must not touch each other, nor touch the walls of the boxes.

On the first layer of iron bars is placed a second layer of carbon, 1 to 3 cm. thick; on this a new series of bars; then more carbon, and so on in this way until the last layer of carbon reaches to within 10 cm. of the upper edge of the box; then the whole mass contained in the box is covered with a layer of already-used cement, and on this is placed a last layer of a refractory powder capable of preventing the access of furnace gases into the interior of the box. Usually, this is the powder formed when pieces of steel are polished or steel utensils are sharpened on siliceous grindstones. This powder is composed of grains of silica mixed with particles of steel, and possesses the property of agglomerating or sintering at the temperature of the cementation furnaces, forming a mass impermeable to gases. This property is probably due to the fact that the particles of steel are oxidized by the action of the furnace gases and form with the silica a partially fusible slag which cements to each other the particles forming the rest of the mass. In many cases simple refractory clay is used for the same purpose. The covering is usually completed with a layer of refractory bricks.

When wood charcoal is used as cement, in the form of powder mixed with small grains the size of peas, the charge is usually made in the proportion of 35 to 45 liters of carbon to 100 kg. of iron. Taking into account the space occupied by the "bottom" of refractory earth and the "cover" of earth and bricks, the space occupied by the iron bars rarely exceeds 35% of the total available space in the boxes.

The trial bars, called *spies*, are placed in the boxes by introducing them through the holes which we saw were made for this express purpose in the outer walls of the boxes and (corresponding with the former) in the outside walls of the working chamber of the furnace. They are put in place during charging when the charge has reached the level of these holes.

The charging of the boxes being finished, the furnace is closed. This, in furnaces with fixed boxes, consists in walling up the working doors and luting with refractory clay the interstices around the trial bars. Then the fires are lit and the temperature of the furnace raised to bright red or yellow heat. This temperature, which corresponds to 1050–1150° C., is usually reached in from forty to sixty hours, according to the dimensions and type of furnace used. Then the temperature is kept constant for seven to eleven days, according to the degree of carburization which it is desired to obtain, taking care to heat the boxes everywhere to as uniform a temperature as possible. This is quite easy when using gaseous fuel, and also in furnaces with solid fuel by regulating, by refractory bricks, the size of the upper openings of the channels through which the gases of the furnace circulate within the boxes.

In general, the judging of the temperature of the furnace is left entirely to the experience of the furnace foreman, who estimates it on the basis of the color of the boxes. It is well known that such an estimate is very uncertain, especially since it depends on the variable conditions of illumination of the plant in which the furnace is placed.

In order to avoid harmful "heat waves," *i.e.*, strong local rises in temperature which may cause the melting and therefore the loss of a part of the iron already carburized, it is sometimes customary to place on the cover of the boxes, or near to them at other points of the furnace, "Seger cones" of different numbers, which serve quite well to regulate the temperature.

Although so accurate and easy to use, I have never seen optical or electrical pyrometers employed in works for the cementation of fusion-steel. The employment of registering pyrometers would be especially easy and advantageous.

As already said, the temperature at which cementation is effected strongly influences the results of the operation. We know that the depth to which the carbon penetrates into the iron in a given time is greater the higher the temperature, so that, at least from the point of view of rapidity of operation and output of the plant, it is profitable to keep the temperature of the furnaces as high as possible, within permissible limits. Too high temperature causes excessive concentration of the carbon and risk of melting the external layers of the partially cemented bars.

Usually, it is considered good practice that the temperature for effecting total cementation must be close to the melting of copper (1085° C.).

If, instead of the usual cement containing a mixture of used and new charcoal, only new charcoal is used, or a more active cement, such as the mixture of carbon and barium carbonate, it is necessary to work at a lower temperature, to avoid too intense carburization; in this case it is necessary to prolong the heating somewhat, in order to extend the carburization to the desired depth.

The length of the heating varies according to the cement used and the product which it is desired to obtain. When the usual mixture of new and used wood charcoal is used, the length of the heating at full heat is about seven days if the steels are to be used directly after simple forging of the separate bars, eight days if the steels are destined for subsequent piling in fagots and forging, nine to eleven days, according to the degree of carburization it is desired to reach, if for steels intended to be melted in crucibles.

But even when always using the same materials, inevitable variations in the temperature of the furnace render necessary direct control of the carburization, so as to be able to interrupt the operation at the proper moment. For this control, the trial bars or *spies* are often placed in the cementation boxes in such a way that they can be removed during the operation. When it is judged that the cementation is reaching its end, one of the trial bars is removed, quickly closing up the hole with refractory luting material. The examination of the surface of fracture of the bar, broken either after slow cooling or after tempering, preceded or not by forging, permits of judging with some approximation the time during which the heating must be continued to obtain the desired degree of carburization.[1] To the examination of the fracture, which necessarily gives imperfect results, is sometimes added a quantitative determination of the carbon in a sample of the metal taken from the external layers of the bar. Results just as rapid, but far more accurate and complete, can be obtained by subjecting to microscopic examination a plane transverse section of the bar allowed to cool slowly. This microscopic examination can be carried out in less than ten minutes, not requiring a complete polishing of the section, and it furnishes directly data of the highest accuracy, both as to the depth the carburization has attained, the maximum concentration reached by the carbon in the bars, and the distribution of the carbon in the mass or its concentration in the various layers of the iron. This last datum is of great importance when the cemented bars are to be used directly, without undergoing such subsequent treatment (*e.g.*, fusion) as is capable of making the concentration of the carbon homogeneous. This knowledge is, in any case, most useful in judging whether it is necessary to change the temperature of the furnace toward the end of the operation.

The reason this test is not usually made is the quite widely diffused, but erroneous, belief that a micrographic examination requires a costly equipment. Such a supposition is entirely unfounded, for the apparatus and the adjuncts necessary to effect a micrographic control of the cementation certainly do not cost more than two or three hundred lire (forty or sixty dollars), and the work of control can be carried out by the workman supervising the furnace, to whom the necessary instructions can be given.

The further duration of the heating is regulated on the basis of the results of the examination of the trial bars, taking into account the fact that after the fires are extinguished a considerable time is necessary before the temperature of the boxes is lower than that at which cementation can take place. This datum, which depends upon the quickness with which the furnace cools and therefore varies from one furnace to another, can be judged only on the basis of previous operations carried out in furnaces of the same type and of the same dimensions.

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[1] It is not possible to describe the structures of the *spies* characteristic of the various stages of the cementation. Only long experience can give skill in recognizing, by examination of their surfaces of fracture, the stage reached by the cementation.

Usually, it requires from four to seven days for the furnace to cool so far as to permit the entrance of workmen to empty the boxes.

The quantity of fuel burned during the cementation varies between very wide limits, with variations in the nature of the fuel itself and with variations in the type of the furnace. In ordinary grate furnaces for the direct use of solid fuels, for every ton of cement steel there is usually burned from 750 to 900 kg. of cannel coal, or from 1600 to 3000 kg. of lignite or peat, or from 3000 to 3500 kg. of wood. In furnaces with wood gas producers, the consumption of this fuel is reduced to about 2000 kg. per ton of cement steel.

The length of an operation, including the time necessary for charging, emptying, repairs, etc., varies, in general, between twenty and thirty days. It is seldom that more than fifteen cementations can be made in one year in one furnace.

The cemented bars are broken and subdivided into groups, in the way I shall describe later, on the basis of the appearance of their surface of fracture. This method of classification is of slight accuracy.

English manufacturers, in general, "classify" the cemented bars into seven groups, or "numbers," according to their approximate carbon content as judged from examination of the fractured bars. The first group includes the least carburized bars, in which the fracture shows very clearly the "nucleus" of unchanged iron remaining; the second includes steels in which the *mean* carbon content is about 0.5%; the bars of No. 3 contain on an average from 0.8 to 1% of carbon; those of No. 4 from 1 to 1.3%; those of No. 5 from 1.3 to 1.5%; those of No. 6 from 1.5 to 1.8%; and those of No. 7 (designated by the name of "doubly converted bars") about 2%.[1] The bars which on account of heat waves in the furnace have undergone incipient surface fusion are classified separately and designated by the name of "glazed bars." Finally, the bars which have undergone superficial refining or oxidation, produced by the entrance of air through cracks formed in the boxes or through badly luted joints in the cover, are also classified in a separate group and are called "*aired bars.*" These superficially decarburized bars are easily recognized, as their surfaces of fracture are characterized by a peripheral zone possessing the characteristic crystalline and lustrous structure of oxidized or "burnt" steel.

It is very difficult to describe, even approximately, the characteristic appearance of the surface of fracture of the cemented bars, and even more difficult to give indications for recognizing from this appearance the approximate carbon content. Only long practice and continuous and attentive observation of the bars of the different classes permits the most able workmen to make a good classification on the basis of this primitive method of observation.

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[1] These products of such high-carbon content are really obtained, usually, by means of two successive cementations.

An inexperienced eye can recognize with certainty only *very highly* carburized bars, from 1.5 to 2% of carbon, by examining the surfaces of fracture of the *non-hardened* bars. These are characterized in such high carbon steels by the presence of many brilliant plane surfaces of cleavage, due to the fact that the fracture is effected chiefly along the brittle laminas of cementite (Fe_3C) which penetrate in great quantity the mass of steels highly carburized by cementation.

Moreover, not all manufacturers make so minute a classification of their products. Many of them begin by leaving aside the bars not sufficiently cemented, those that remain almost as malleable as the original iron, and those which have undergone a more or less deep refining; both the former and the latter are subjected again to another cementation. Then they also leave aside the bars which have undergone incipient fusion, and limit themselves to subdividing the others into three groups, according to their degree of carburization.

As regards the appearance of the external surface and of the surfaces of fracture of all cemented bars in general, two essential characteristics are present, easily recognized even by those who have not such an experienced eye as is necessary to make the classification to which I have just referred. The first consists in the fact that the surface of cemented *wrought iron* bars no longer has the metallic appearance, the continuity and the uniformity which the iron bars had before the cementation; but it is coarsely opaque, of brown color, and covered with "blisters" or "beads" varying in size from a pea to a walnut, scattered over the whole surface of the bars.

It is considered an indication of good quality in the product when these "beads," "bubbles" or "blisters" are small, uniform, uniformly distributed over the surface of the bars, and especially when they do not collect in marked abundance along definite lines.

To these characteristic blisters are due the names by which cement steel bar is designated in various languages. Thus, in English it is called *blister steel;* in French, *acier poule;* and in German, *Blasenstahl.*[1]

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[1] In the report containing propositions for "a uniform nomenclature of iron and steel" presented in September, 1909, by M. H. Howe and A. Sauveur before the Congress of International Associations for Testing Materials, *acier poule* or *blister steel* is defined simply as "steel obtained by carburizing wrought iron (*ferro saldato*) by heating it in contact with substances rich in carbon," and it is added that "it can likewise be obtained by carburizing a steel of low carbon content."

The authors of the report consider that any steel obtained by cementation should be called *blister steel* or *acier poule*, whether it shows the characteristic blisters or not.

As to the origin of the blisters or "beads" characteristic of steel obtained by cementing *wrought iron*, many different hypotheses have been advanced; but the knowledge of their causes would have no importance for practice, because the phenomenon does not occur in those cases in which it would produce the most harmful effects, that is, in the partial cementation of objects of cast steel which are not to undergo any other treatments after the cementation other than hardening and fitting.

In general, the tendency to-day is to regard as correct the hypothesis proposed by Percy as early as 1864. According to this, the "blisters" are formed by the local evolution of carbon monoxide, formed by the action of the carbon which diffuses into the iron on the slag, rich in oxides, contained in the form of specks in the iron. As is seen, this hypothesis in its simplest form, presupposes that the carbon diffuses into the iron as such and not in the form of carbon monoxide. Therefore, assuming that we now know that the penetration of the carbon occurs chiefly by the agency of the diffusion of carbon monoxide into the iron, Percy's hypothesis needs some modification.

It does not seem that there can be any doubt that the formation of "blisters" is due to the presence of slag. In fact, as early as 1878 Percy showed that if iron is subjected to cementation after having been fused, so as to eliminate the slag, the "blisters" are no longer produced, although the cementation proceeds, in all other respects, in exactly the same way as when ordinary iron is used. Moreover, as previously stated, the surface cementation of finished objects of fused soft steel, destined not to undergo further forging or fusion, is possible just because of the fact that with this material, totally (or almost entirely) free from slag, the "blisters" are not formed.

The second easily recognizable characteristic of the structure of cemented bars of soft iron or steel consists in the fact that their structure varies markedly from the outside to the center. For example, a bar quenched at about 800° in cold water and then broken, shows the "grain" of the surface of fracture fine and compact (though of variable fineness and compactness) at the outer edge and for a portion corresponding to over 0.4–0.5% carbon; within this zone and to the center of the bar, the metal gradually resumes its original characteristic crystalline structure.

This variation in the "grain" of the metal from the periphery to the center of the cemented and hardened bar gives approximate indications as to the "depth" reached by the cementation; but, as we shall see better later, the results which are thus obtained correspond only within quite wide limits with the precise data furnished by the microscopic examination of the suitably etched and polished sections, or by the chemical analysis of the material obtained from successive layers of the bars. This must be taken into account when it is desired to estimate, from the examination of the trial bars or "spies," the point to which the cementation has progressed.

The only precise information which can be obtained from these observations is the absence or the presence of the "nucleus" with crystalline structure; if absent, the bar is certainly "core" cemented, while if present the carburization has not reached to the center of the bar and is limited to a more or less deep enveloping zone.

The real distribution of the carbon in the deep cemented zones, as found by chemical analysis of successive layers, has been already discussed in the first part of this book, referring there to various practical data. To complete what was there given, we will report here some data relative to other industrial cementation operations; a comparison of these with those before given will show still more clearly the strong variations which small differences in the conditions of working, such as temperature, composition of the cement, etc., produce in the results of the operation.

The data contained in the following table are due to Bildt, and refer to a bar of Lancashire iron cemented with a mixture of sixty parts wood charcoal and forty bone ash, for thirty hours at 1100°–1200° C.

Depth (mm.)	Carbon, percent.	Depth (mm.)	Carbon, percent.	Depth (mm.)	Carbon, percent.
Surface	1.0	3.0	0.35	6.2	0.09
0.8	1.0	3.8	0.12	7.0	0.045
1.5	0.8	4.6	0.11	7.7	0.040
2.3	0.5	5.4	0.10	...	.....

The table which follows reports the results of analyses of successive layers made by Arnold[1] on cemented bars classified, according to the standards of English manufacturers to which I have already referred, by the numbers 2, 3 and 4. The last column contains the data relative to a bar of No. 4 which had undergone incipient refining, an *aired bar*.

Layer	Depth (inches)	Percent of carbon			
		Bar No. 2	Bar No. 3	Bar No. 4	Bar No. 4, refined
1 (surface)	0.02	0.98	....	....	....
2	0.04	0.95	1.40	1.50	....
3	0.06	0.76	....	....	0.30
4	0.08	0.63	1.26	1.45	1.20
5	0.10	0.50	....	....	1.45
6 (middle)	0.12	0.39	1.15	1.27	1.45
7	0.14	0.37	....	....	1.45
8	0.16	0.31	1.10	1.29	1.40
9	0.18	0.18	....	....	1.38
10	0.20	0.15	0.98	1.29	1.38
11	0.22	0.10	....	....	1.35
12 (center)	0.24	0.10	0.88	1.15	1.16
Mean carbon content......	....	0.45	1.13	1.33	1.04

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[1] *Journal of the Iron and Steel Institute*, 1898, Vol. II, p. 185.

In the bars of Nos. 5 and 6 (from 1.4 to 1.8% of carbon), the concentration of the carbon does not vary appreciably from the periphery to the center.

As to the composition as a whole of the cemented steels, it is, aside from carbon, quite similar to that of the iron used, as the cementation can not give rise, to a marked degree, to any other effect (neglecting the probable penetration into the steel of small quantities of nitrogen, coming from the air occluded in the cement or from the cement itself) than that of raising the carbon content of the iron used as raw material.[1]

The table which follows gives the results of analyses of some cement steels reported by Wedding:

No.	Quality and source of cemented steel	Amorphous C, (a) per cent.	Graphitic C, percent.	Si, percent.	P, percent.	S, percent.	Mn, percent.	N, percent.
1	From Elberfeld, soft.	0.416	0.80	....	....	....	....	....
2	English, forged and hammered cold.	(Total C—1.87)		0.10	....	....	....	....
3	English, forged and hammered cold,	0.627	0.105	0.03	....	0.005	0.120	....
4	English, forged.....	1.20	0.30	....	....	....	....	0.016
5	English, forged.....	1.24	0.30	....	....	....	....	....
6	English, hardened. .	1.48	0.02	....	....	....	....	0.016

(a) Includes, evidently, the hardening and carbide carbon.

And I add, in the table which follows, the data reported by Helson (*La Sidérurgie*) relative to the composition of three French cemented steels:

	I	II	III
Carbon	1.750	1.200	0.960
Silicon	0.063	0.055	0.060
Sulphur	0.004	0.004	0.007
Phosphorus	0.007	0.013	0.013
Manganese	0.030	0.050	0.070

From these data and from those already given relative to the composition of the types of iron most frequently used for the manufacture of cement steel, it is evident that in reality cementation does not appreciably modify the composition of the metal except by increasing the carbon; this explains the great purity of the steels which can be obtained with this process. This purity is perhaps the only reason for the better quality of the steels obtained by carburizing pure wrought irons *without melting them*, and therefore the cause of the survival of this industry.[1]

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[1] The weight of the cemented steel is, in general, about 0.5–0.75% greater than that of the iron used to make it.

As regards the state in which the carbon is present in the cemented steels, I reproduce the following data, reported in part by Ledebur[2] and in part by Thallner.[3]

No.	Quality and source of cemented steel	Hardening carbon, percent.	Carbide carbon, percent.	Annealing carbon, percent.	Total carbon, percent.
1	Steel from the Bismarckhütte with very coarse grain (Thallner).	0.66	0.82	....	1.48
2	Steel from the Bismarckhütte with coarse grain (Thallner).	0.60	0.82	....	1.42
3	Steel from the Bismarckhütte with fine grain (Thallner).	0.745	0.765	....	1.51
4	Id. (Thallner)......................	0.68	0.63	....	1.31
5	Steel from the Bismarckhütte with very fine grain (Thallner).	0.54	0.47	....	1.01
6	Steel from Remscheid (Ledebur)........	0.19	0.97	0.04	1.20
7	Swedish steel (Ledebur)...............	0.42	1.07	....	1.49

It is seen from these data that cemented steels of these types do not contain annealing carbon (except traces in No. 6), a fact which accords well with their very low silicon content. The relation between the quantity of hardening carbon and that of carbide carbon depends naturally on the thermal treatment to which the steel has been subjected. Thus, from the numbers of the preceding table, it follows that while Steel No. 6 has been allowed to cool slowly in the boxes below the temperature of hardening (first critical point), the others have been removed from the boxes while they were still red hot and then suddenly cooled.

As I have already said, it is seldom that the cemented bars are used directly,[4] on the one hand because of the "blisters" and on the other on account of the non-homogeneous distribution of the carbon which ordinarily results from the process of cementation. The maximum differences in carburization are observed between the ends and the central parts of the bars, the former being always more carburized than the latter, and between the periphery and the "nucleus." Moreover, there are often present, even in bars contained in the same box, strong "accidental" variations in carburization, due to non-uniform heating of the various parts of any box, imperfect contact of the iron with the cement at given points, etc.

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[1] The investigations of Boussingault, already referred to (see p. 23), would show that cementation, carried out under the conditions usual in industry, reduces the sulphur content in the iron treated; a reduction which may sometimes amount to as much as 80% of the initial sulphur content. According to the same investigations, the phosphorus and silicon contents, on the contrary, undergo a very slight increase, which may be attributed to the action of the ashes of the wood charcoal used as cement. It is a question, however, in these last two cases, of phenomena which, owing to their very small extent, have no practical importance.

[2] *Handbuch der Eisenhüttenkunde*, 4th edition, p. 1085.

[3] *Stahl und Eisen*, 1899, II, p. 914.

[4] Cemented bars, subjected to only a simple forging or rolling, constituted for a long time the material most commonly used for the manufacture of springs. English manufacturers, in fact, called the material thus obtained *spring steel.*

In these cases, where a product of perfect homogeneity is not required, it is sufficient to pile pieces of sorted bars into packets or bundles, which are then subjected, one or more times, to heating in hearths or in reverberatory furnaces and to forging or rolling. We can not enlarge here on the details of these operations; they are applied, as is well known, to steels of most varied sources, and form an important operation of the general metallurgy of iron. We will merely mention the necessity of always heating the packets and the bars in a neutral atmosphere and under the protection of a slag or of clay, so as to avoid decarburizing the steel. Notwithstanding these precautions, however, the finished product is always less carburized than the bars used, and only long practice permits of selecting the bars of the "grade" adapted for obtaining a definite product. The steels obtained by the re-heating and forging of packets of cemented bars are still to-day largely used for the manufacture of cutlery of all kinds.

When, on the contrary, it is desired to obtain a product perfectly homogeneous and free from slag, recourse is had to fusion of the cemented bars; this is almost always done in crucibles,[1] but has quite recently begun to be done in electric furnaces.

Of this process, also, it is not in place here to give detailed information, for while the technology of this process has nothing to do with that of cementation proper, its applications, extending to the fusion and manufacture of steels obtained by processes different from cementation, would lead to a chapter of the metallurgy of iron which has nothing to do with cementation. On the other hand, excellent and exhaustive treatises on the processes of crucible fusion of steel are to be found in many treatises on iron.

We will, therefore, report in the following table only the chemical analyses of three steels obtained by fusing cement steels in crucibles, simply to show within what limits this last treatment influences the composition of those cement steels whose greatest value is their purity.

The numbers reported below are taken from the paper of Thallner already quoted from:

	No. 1		No. 2		No. 3	
Carbon	1.31	percent	1.44	percent	0.96	percent
Manganese	0.14	"	0.14	"	0.13	"
Silicon	0.05	"	0.10	"	0.09	"
Phosphorus	0.010	"	0.015	"	0.012	"
Sulphur	0.003	"	.....	......	.....	......
Copper	0.011	"	.....	......	.....	......

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[1] As we have already seen (see p. ix), the invention of the process of crucible fusion of steel is due to Benjamin Huntsman (1735–1740).

As is seen, the product obtained by crucible fusion preserves almost unchanged the purity of the cement steel fused.

It is well to point out that it is difficult to avoid oxidation during the fusion and the formation of blowholes when casting steels of the composition of those indicated above. So that, usually, in charging the cement steel to be fused there are added de-oxidizing alloys such as ferro-manganese and ferro-silicon, adapted to furnishing a de-oxidized steel without blowholes. This is the reason why crucible-fused cement steel usually contains more manganese and silicon than is normally found in the raw materials. It is true that sometimes the reason for the higher content of manganese and silicon is quite different, and is simply the fact that the steel sold as "crucible-fused cement steel" is not such, but comes from the Bessemer converter or the open-hearth furnace!

In the crucible fusion of cement steel, the desired "grade" or carbon content is obtained either by charging into the crucible pieces of accurately classified cement bars, all chosen of the necessary homogeneous grade, or by charging bars of a higher grade and then suitably lowering the carbon content by the direct addition of softer bars or of iron itself.

As regards the cost of cement steel, it is easy to understand that it is not possible to furnish in general precise data because of variations in the local and temporary prices of the raw materials and in labor, fuel, refractory materials, etc. From the data of many works in which the production of cemented steel is carried out on a large scale we may consider as the minimum 45 lire ($9) and the maximum 110 lire ($22) per ton of steel produced. We mean to indicate by this the sum to be added to the price of the raw material (soft iron or steel in bars) to obtain the "industrial" cost (including, that is, labor, depreciation, repairs, general expenses, etc.) of the bars of cemented steel in the state in which they are removed from the cementation boxes.

As an example may be cited the cost of cementation in the basin of the Loire, which still produces considerable quantities of cement steel for fusion. This cost oscillates on the average between 55 and 80 francs ($11 to $16) per ton of product.

The use of gaseous cements, proposed by MacIntosh in 1825 (see p. xiii), has found wide application in the processes of partial cementation but has not given good results in total cementation, so that to-day it may be considered as abandoned in the industry of the cementation of wrought iron bars to steel.

On the contrary, the processes of cementation based on the use of mixed cements, solid and gaseous, have found wide application, even for making cement-steel for fusion, especially owing to the fact that they give very rapid cementation and guarantee absolute purity of the product. But the introduction of these processes has not yet extended as far in the production of fusion steels as in the production of partially cemented steels.

CHAPTER II

PARTIAL CEMENTATION OF WROUGHT IRON AND SOFT STEEL

Reference has already been made in the first part of this volume to the development of the industrial process of the partial carburization of objects of soft iron or steel. The recent enormous development of machine technology and the more difficult and complex conditions which the metals required by this industry must satisfy are the causes of the wide diffusion and increasing importance of the processes of partial cementation. It is such processes alone which make it possible to combine, in one piece of steel, surface hardness with high tenacity, and to harden effectively, without serious difficulties and risks, objects which could not be easily hardened if made wholly of hard steel.

We will describe briefly industrial practice for the execution of these processes.

The rational conduct of the individual operations follows in a simple and precise manner from the considerations developed in the first part of this volume; the object of this chapter is to show what are the material conditions best suited to realize these rules in practice in the simplest and surest way.

In the several sections of this chapter we will deal separately with the conditions of use of individual "types" of cements, and with "special" processes of cementation whose application is radically different from those of all other processes.

§1. GENERAL CONSIDERATIONS

The processes of partial cementation, or "superficial cementation," are designated in English, in German and in French by the respective terms: *case-hardening*, *Einsatzhärtung* and *trempe à paquet*, and sometimes in Italian by a name too literally translated from the French: *tempra a pacchetto*. They are almost exclusively used for the surface carburization of objects of soft or low-carbon steel completely or almost completely finished, or at least of pieces which have already undergone, in the parts which are to be cemented, all the necessary treatment with cutting tools and which are only to be machined later, if necessary, on the emery wheel.

Save for a few rare exceptions, the essential practical purposes of surface cementation are four:

(*a*) To obtain, after quenching, pieces of steel which are not brittle and possess sufficient surface hardness to prevent rapid wear by friction. Such is the object of treating toothed wheels for gearing, axles, cams and rods of valve gears, and a large quantity of machine parts destined to stand both friction and considerable strains, such as flections, shocks, etc.

In the greater part of these cases the cementation is limited to a thin surface zone, and the thermal treatment to which the piece is subjected afterward must be studied with the greatest care with the ultimate objects in view of making the cemented zone hard and of giving the maximum tenacity to the "heart" of the piece, thus neutralizing the harmful effect produced by the long heating in the cementation process.

(*b*) To render possible, or at least easier, the efficient hardening of pieces of large dimensions and of complicated and irregular form which, if they were entirely of steel of high carbon content, would be exceedingly difficult to harden without the production of fractures or cracks.

(*c*) To render considerably less the cost of steel objects in which the parts which are to "take the hardness" constitute only a small portion (in general, the outside portion) of the total mass. This is attained by the smaller cost of the raw material and the smaller expense of machining the softer material.

(*d*) To obtain at low cost pieces of steel capable of taking a beautiful polish.

The quality of the raw materials used for pieces intended to be cemented superficially naturally varies within very wide limits, according to the purposes for which these pieces are to be used. It is not possible to establish general rules in this respect. We will take occasion later to cite some concrete and precise data in some special cases.

Whenever it is not necessary that the soft nucleus should possess special qualities of resistance to shock and stress (such is, for example, the case for many cutting utensils), ordinary carbon steel is used as raw material, for reasons of economy. It may be specially noted that, contrary to what is considered good practice in the case of the total cementation of materials intended to be fused or strongly forged after the cementation (see p. 203), it is advantageous, and in many cases necessary, to use steels proper, obtained by fusion, instead of puddled or wrought irons. This might be considered evident *a priori*, when we remember that the presence of veins and granules of slag would not only be in itself a detriment in any piece subjected to strong friction or to other localized forces, but it would give rise to deep-seated irregularities in the cementation and is also the principal, if not the sole, cause of the formation of "blisters" (see p. 215), which would render useless a piece not further worked hot but used practically as it is. Practice confirms the fact that the use of fused steels, free from scoriæ, avoids the formation of the blisters.

In those cases in which it is necessary that the soft nucleus of the cemented pieces should possess maximum tenacity, it is well to use as raw materials soft nickel steels instead of the ordinary carbon steels, since even after carefully executing the thermal treatment most effective in "regenerating" the soft metal of the nucleus, it is difficult to obtain fully satisfactory results with plain carbon steels. The soft nickel steels most frequently used for this purpose are those containing 2 to 3% of nickel, which are cemented under practically the same conditions and according to the same rules as carbon steels, and in which the increase in brittleness due to the prolonged heating in cementation is much less marked than for carbon steels. Moreover, for these special steels the "regeneration" of the metal of the nucleus, by means of thermal treatment carried out after the cementation, is considerably more effective and easy. In some cases steels with 5% of nickel are also used; quite rarely steels of higher nickel content. For steels containing more than 4.5–5% of nickel, the phenomena of negative hardening begin to manifest themselves, especially when the carbon content of the cemented zones is rather high.

The use of complex steels different from those just mentioned is limited to special cases, of which we will give an account later.

A large number and variety of "cements" have been adopted in the practice of these processes. The results of recent investigations have confirmed the opinion of the earlier experimenters that the addition of foreign substances to the carbon used as cement serves to increase its efficacy, making the process of cementation more rapid.

But the most precise, and therefore most reliable, experiments show that only *some* classes of substances, acting on iron together with carbon, exercise on the metal an intense carburizing action, and among these substances the only one capable of acting under well-defined and exactly controllable conditions is carbon monoxide. It is not possible to adduce any well-founded reason for the use of the bizarre and complicated mixtures which many technologists employ at the present time, considering them as possessed of marvelous efficacy and jealously guarding the secret of their composition.

Some of these curious mixtures are still recommended to-day in serious treatises, and protected by costly patents. In the present chapter we will deal only with processes based on the use of rational cements, whose mode of action has been widely studied and controlled in practice, such that their use permits of obtaining, when working under well-defined conditions, much more definite and sure results.

Since the technique of the processes of cementation varies greatly, especially with variations in the state of aggregation of the cement, I have considered it well to subdivide the material of this chapter, collecting in the individual parts whatever concerns the technical applications of the cements used in a definite state of aggregation.

We will therefore treat separately of the solid, liquid, and gaseous cements, and of the "mixed cements," meaning by this last designation those cements formed of carburizing substances belonging to two or more different classes, acting simultaneously. In practice, the only mixed cements used consist of combinations of solid cements and gaseous cements.

For the various cements of each of the classes indicated above, almost identical apparatus and methods of procedure are used in practice; this will greatly shorten the subject matter of the present chapter, making it possible to avoid many repetitions.

We will refer separately to a group of special processes based on the phenomena of diffusion of elements other than carbon into solid iron, and to the processes of cementation of armor plates.

§2. SURFACE CEMENTATION WITH SOLID CEMENTS

The technique of superficial cementation with solid cements is extremely simple to describe, but in practice it must be carried out with the greatest care, as the least error in placing the pieces in the boxes, in filling their interstices with the cement, etc., is sufficient to give rise to the most serious defects in the product obtained.

On account of the extremely variable properties of the solid cements which are found in commerce, much practice is needed in the individual cases to be sure of obtaining precisely the desired results. This, in fact, is the principal difficulty in these processes, which are nevertheless so widely applied at present.

Save for rare exceptions, cementation with solid cements is carried out by placing the pieces of steel in "cementation boxes" of cast soft steel or of sheets of soft steel bolted and joined by means of hinges. Boxes of autogenously welded sheets are also sometimes used.

The boxes of cast steel cost somewhat more than those of sheet steel and can not, in general, be made as light as the latter; as an offset, the life of the former is greater, if well constructed.

The life of the cementation boxes depends greatly on the temperature at which cementation is effected, the composition of the atmosphere of the furnace in which they are placed, and the treatment to which they are subjected during the charging and discharging of the furnace. By cementing at 900°-950° C., in a gas furnace with not too strongly oxidizing atmosphere, charging the boxes in the furnace and removing them from it with the greatest care, placing the boxes as soon as removed from the furnace on a layer of fire clay and at once piling up a part of this against the sides of the boxes so as to protect them from oxidation, a box of bolted sheet steel of the average normal dimensions (30 × 35 × 60 cm., with walls 10 to 15 mm. thick) should last for twelve to fifteen operations. Under the same conditions, a box of cast steel, with sides 20 to 25 mm. thick, may serve for fifteen to twenty operations. By using furnaces with distinctly reducing atmosphere, such as are, for example, the modern heavy-oil furnaces, the life of the boxes may be markedly increased.

The boxes must in any case be furnished with a cover of iron or steel (cast or sheet), with the edges shaped so as to fit over the box and insure good closing.

The dimensions of the boxes must be such that the objects to be cemented are contained in it easily, so that there may be at every point a free space of not less than 3 to 4 cm. between their furthest projecting points and the wall of the box. This is for the purpose of providing a layer of cement around these salient points thick enough to insure a uniform cementation.

It is always advantageous, however, to give to the boxes the minimum dimensions compatible with these conditions, because the larger the box the longer the time necessary for the heat to penetrate from the outside to the center, and, therefore, for the temperature to become uniform throughout the box. Some of the disadvantages of slow propagation of heat from the outside to the center of too large boxes are: 1. Marked deformation of the cemented pieces, due to the fact that they are heated for a long period of time to different temperatures in different parts. 2. Marked irregularities in the cementation, which is a maximum in the parts of the pieces nearest to the walls of the box and a minimum, sometimes almost null, in the parts nearest to the center of the boxes. 3. Great length of time necessary to obtain a given cementation.

The disadvantages just enumerated vary with the properties of the cement used and the type of furnace available. They are greater the lower the thermal conductivity of the cement and the smaller the quantity of heat furnished to the working chamber of the furnace in the unit of time at a given temperature. It is not possible, therefore, to give quantitative data of value on this topic; we will quote later some particular examples which will furnish concrete data.

Besides these considerations, boxes of large dimensions are difficult to manipulate and, when they reach certain sizes, can be removed from the furnaces only by means of special and expensive mechanical arrangements, difficult to provide in small plants.

Even for the cementation of pieces of rather large dimensions (toothed wheels, sectors, axles, etc.) it is not desirable to use boxes longer than 55–60 cm., nor wider than 45 cm., nor higher than 30 cm. If the pieces to be cemented can not be contained in boxes of these dimensions, it is advsiable to carry out the cementation in fixed built-up chambers. This can be done (although it is not without its disadvantages) even when using solid cements, but considerably better with gaseous cements or with mixed cements.

When the pieces to be cemented are of small dimensions (axles for bicycles, rings and cups for small ball bearings, links for chains, etc.) it is better to employ much smaller boxes, such as parallelepipedons 30 cm. long by 25 cm. wide and 25 cm. high. Boxes of cylindrical form recommended by Guillet,[1] whose diameter must be 10 to 12 cm. greater than that of the pieces which are introduced into them, are sometimes used; but, although they can be obtained easily and at low cost by making them from drawn steel tubes, and although their form is certainly the most rational and that which permits of obtaining the most homogeneous cementations, they are less easy to charge and to empty than those in the rectangular form.

In charging the boxes it is necessary to take care that the cement is in good contact with the entire surface of the pieces to be cemented, and that the layer of cement surrounding them has in no case a thickness less than about 2 or 3 cm. For this purpose the bottom of the box is first covered with a wash of clay made into paste with water; this is well dried before further charging. Then a layer about 4 cm. thick of the finely powdered and well dried cement is placed upon this, carefully compressing it. On this is placed a first bed of the articles to be cemented, arranging them in such a way as to leave between them free spaces of at least 3 cm. Then all the free interstices between the pieces are carefully filled by pressing in the cement, and afterward a layer of cement of sufficient thickness to cover by 2 or 3 cm. the highest parts of the pieces. If sufficient space remains above this, a second series of pieces is placed upon it, repeating the operations indicated for the first series. The last series of pieces to be cemented must be totally covered by a layer of cement at least 4 cm. thick. If the box is not completely filled, as much cement is placed over this last layer as is necessary to fill the box to the edge; then the cover is put in place, carefully luting all around with the usual fire-clay lute.

The box thus prepared can be placed directly in the furnace, taking care to leave it for some time near the door or at a point not too hot, so as to dry the lute well and to allow the small quantities of water vapor, due to imperfect drying of the materials used, to escape slowly.

The furnaces at present most frequently used for the cementation are those heated by illuminating or gas-producer gas, as this means of heating permits of easy and proper regulation of the temperature, and of obtaining a uniform heating throughout the whole laboratory (working space) of the furnace. Furnaces heated by means of the combustion of mineral oils have recently been introduced into practice, and in some works there are still in use furnaces heated directly by solid fuel (*coal* or *coke*). It seems well, therefore, to make some reference to these different types of furnaces.

Whatever the fuel used, a furnace intended for cementation must satisfy some general conditions which, for cementation with solid cements, may be summarized as follows:

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[1] *Mém. de la Soc. des Ing. Civils de France*, February, 1904, p. 193.

The temperature in the laboratory must be able to easily reach 1100°–1200° C. and must be capable of being kept constant during a practically indefinite time at any point between 850° and 1100° C. For any temperature comprised within this interval, it must be possible to obtain so uniform a heating of the whole chamber of the furnace that differences greater than 30° do not exist between various points in this chamber, except, perhaps, in a small zone nearest to the door. In good gas furnaces the maximum differences in temperature in the body of the furnace when in operation are less than 20°, and sometimes even below 10° C. The atmosphere of the laboratory of the furnace, when in operation, must be nearly neutral, but rather reducing than oxidizing.

To obtain maximum uniformity of temperature in the laboratory of the furnace, it is well that the flames should bathe the walls and the arch of the laboratory itself, coming as little as possible in contact with the boxes, so that the latter are heated indirectly by heat reflected from the walls and the arch of the furnace and not by direct contact with the flame or hot gases.

In large furnaces, heating the whole laboratory to a perfectly uniform temperature is sometimes difficult. Guillet proposes to consider the laboratory of the furnace as subdivided into various zones, in each of which the temperature maintained is of the required degree of uniformity. By determining the mean temperature of each of these regions for a given operation of the furnace, and being careful to take into account the region in which each of the cementation boxes is placed, it is possible to know approximately the temperature at which the cementation is being effected in each box.

The doors of the furnace must close well and must be furnished with one or more holes, 2 or 3 cm. in diameter, to permit of taking samples of gas, of observing the interior, and of measuring the temperature by a pyrometer without opening the doors. These holes must usually be closed by means of clay stoppers.

The height and the width of the doors of the furnace must exceed the height and the width of the cold cementation boxes by at least a couple of centimeters; otherwise it may be difficult, or even impossible, to remove the boxes from the furnace after the heat has expanded them.

In general, portcullis or lift doors, balanced by counterweights, are preferable to doors mounted on hinges. In fact, the former, even when opened, are considerably less cumbersome, and always present to the workman their cold side, while hinge doors, when opened, present to the workman their incandescent side, enormously increasing the discomforts due to heat radiating from the furnace.

An arrangement which greatly facilitates the charging of the furnace is the roller, as long as the width of the door, placed horizontally immediately in front of the door in such a way that it projects 5 or 10 mm. above the level of the floor of the laboratory and of the sill of the door. The boxes are slid on this roller, or the bars of iron on which the boxes are placed, both for introduction and removal from the furnace, are rested and moved on the rollers.

The charging and the discharging of the boxes is facilitated in furnaces having a movable body mounted on a car which can be removed from the furnace with its whole charge. This arrangement is, however, rarely used in furnaces of small or medium dimensions, in which the difficulties of charging are not such as to justify the greater complexity and the greater cost of equipment and maintenance which the movable body entails. It is, on the other hand, now adopted almost always in furnaces intended for the cementation and the thermal treatment of large sized pieces, such as armor plate.

Section a-b.

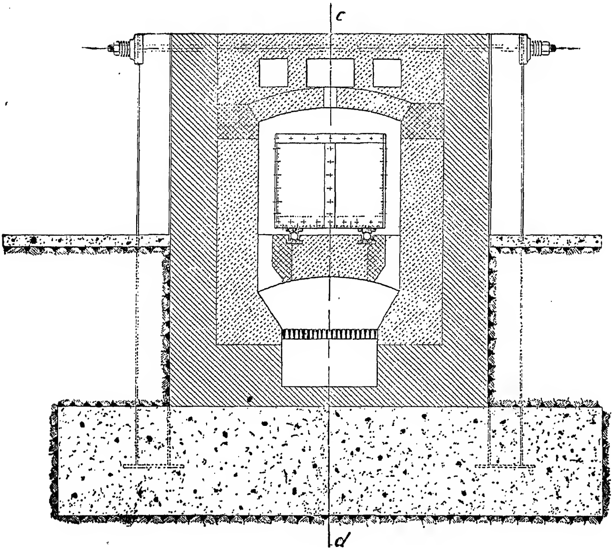

FIG. 79.

Furnaces in which solid fuel is used *directly* for heating are at present little used, on account of the greater difficulty of obtaining a uniform heating of the whole masses contained in the laboratory and in avoiding the so-called "heat-waves" or sudden rises in temperature which may ruin the entire charge of a furnace. Moreover, in furnaces heated directly with solid fuel it is not possible to avoid the considerable oscillations on the temperature occurring every time fresh fuel is put on the grate. These oscillations, as we have already seen,[1] are the cause of great modifications (difficult to foresee *a priori*)

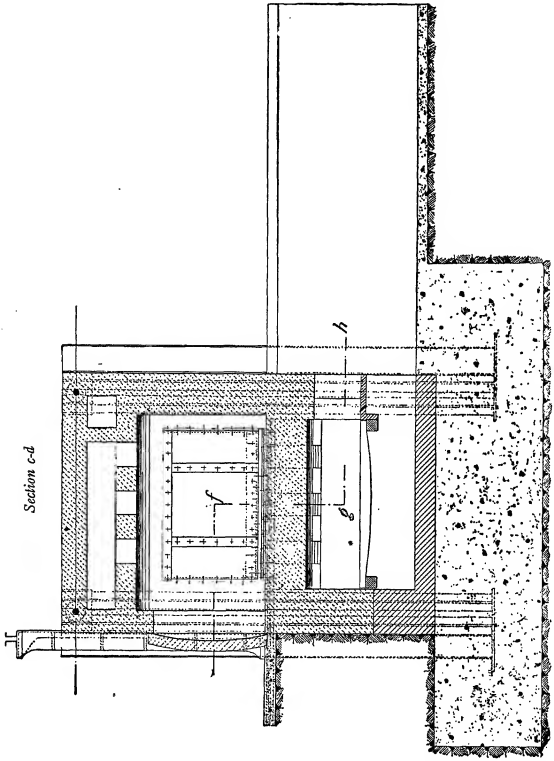

FIG. 80.

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[1] See p. 159, *et seq.*

in the properties of the cemented zones which are obtained. This is a serious obstacle to the proper conduct of the operations following cementation, and a permanent menace of total failure.

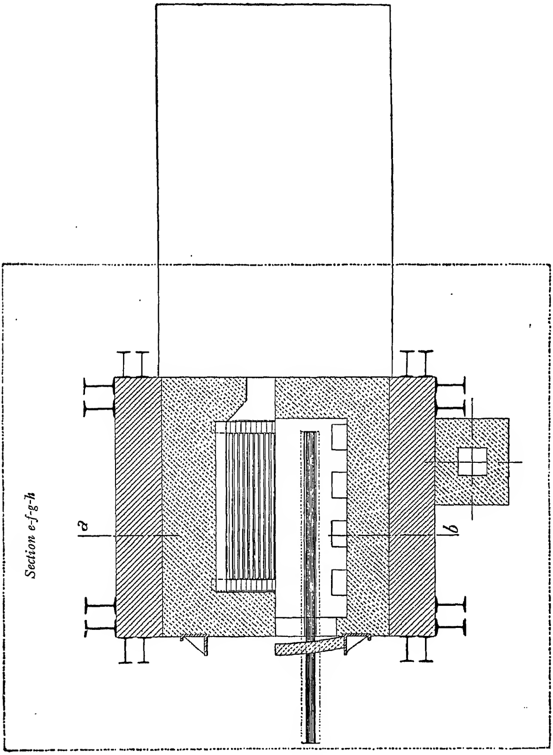

Fig. 81.

Nevertheless, furnaces using solid fuel are still found in small cementation works on account of the low cost of equipment and operation, so that it seems well to make a brief reference to the more common types.

Figs. 79, 80 and 81 represent three sections of one of the simplest types of furnaces using solid fuel for cementation in boxes. The figures are sufficiently detailed to render further explanation superfluous. A damper permits of regulating the temperature.

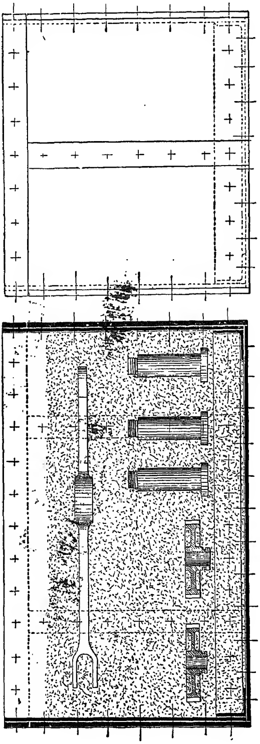

Fig. 82.

Figs. 82 and 83 indicate schematically the structure and the manner of charging a box.

For very long operations, lasting over forty-eight hours, furnaces are sometimes used with fixed boxes of refractory bricks. With these furnaces, similar to those described in connection with total cementation (see p. 207), the operations of charging and discharging are greatly facilitated if the furnace is supplied with a movable arch, like that shown in Figs. 84, 85 and 86.

These figures, also, do not require any description; we call attention to the distribution of the holes *a a*. . ., in the arch, designed to regulate the temperature in the various parts of the chamber by closing them more or less in such a way as to obtain maximum uniformity of heating.

The fuel best adapted to these furnaces is ordinary gas works coke.

Another furnace with solid fuel, adapted to the cementation of small pieces and recommended for its low cost of equipment, is shown in three sections in Figs. 87, 88 and 89.

The cementation boxes are introduced into the first chamber, immediately above the hearth. When this is kept at 1000° C., the usual temperature at which the cementation is effected, the gases which issue from it, passing through the second chamber, situated above the first, heat it to a lower temperature, varying usually between 650° and 800° according to the fuel used, the dimensions of the various parts of the furnace, etc. This second chamber, which re-covers part of the heat which would otherwise be lost, can be usefully employed for heating the pieces before and after cementation.

The furnaces of which I have thus far spoken are fixed. There are also constructed portable coke furnaces, which in many cases are more convenient than the preceding.

One of these furnaces, constructed by Wilhelm Hertsch of Stuttgart, is represented in perspective in Fig. 90, in longitudinal section and in transverse section in Fig. 91. It is constructed in sizes varying between 210 and 800 mm. in the width of laboratory, between 120 and 600 mm. in its height and between 320 and 1200 mm. in its length. It permits of uniform heating, using simple chimney draft, up to a temperature of 1000° C., taking boxes whose dimensions must be at least 50–60 mm. less than the corresponding dimensions of the laboratory.

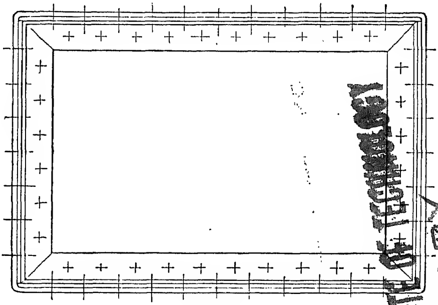

FIG. 83.

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The same manufacturer constructs furnaces of a similar type of much greater dimensions, and also with two or more chambers placed one next to the other or one above the other.

In furnaces with very long chambers, such as that represented in Fig. 92 (the working laboratory of which is 5200 mm. long, 350 mm. wide and 250 mm. high), the uniformity of the temperature is obtained by means of several fire-places placed on the sides. Furnaces of these dimensions are no longer movable, but must be fixed and walled in place.

Special types of furnaces are necessary for cementation with solid cements when it is desired to use liquid fuels (hydrocarbons).

The use of furnaces employing liquid fuel has spread very rapidly in the United States of America and is spreading in Europe, especially for small plants intended for intermittent operation. In plants of this kind, where it is necessary that the fires be extinguished every evening and the furnaces be rapidly put into operation the following morning, it is not possible to use furnaces built like those for producer gas, which, because of their considerable mass and that of the gas producers and heat regenerators necessary, are adapted only to *continuous* operation. In these cases also, furnaces using solid fuel *directly* on grates do not give good results, on account of the considerable time which they always require to be lighted and put into operation. The only furnaces which are well adapted for small plants intermittently operated are those burning illuminating gas or liquid hydrocarbons. The

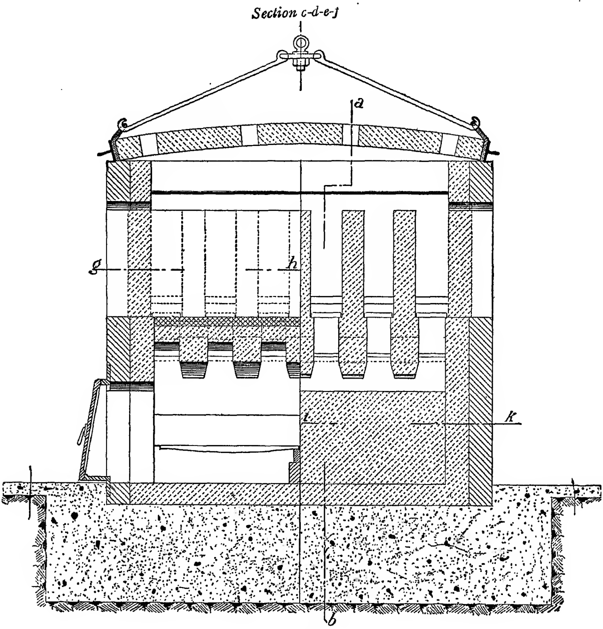

FIG. 84.

former presuppose that the works has a supply of illuminating gas; at times, through special conditions, illuminating gas can be obtained at an extraodinarily low price, but in almost all cases it will be considerably less economical than the burning of liquid hydrocarbons.

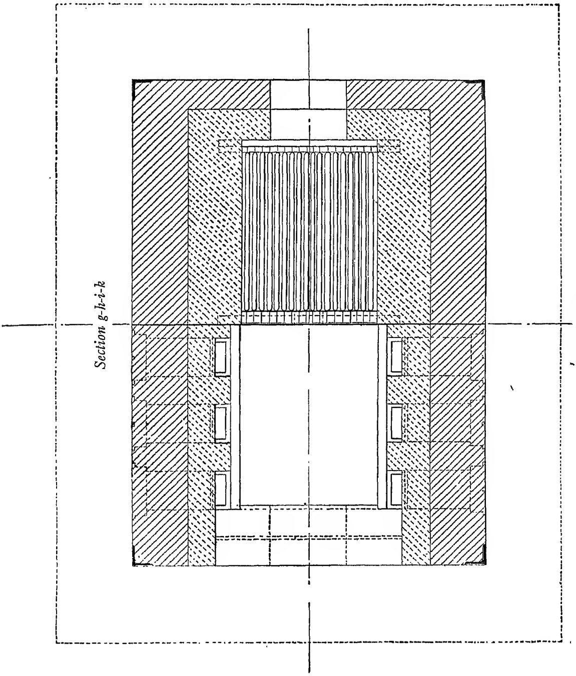

FIG. 85.

Among the many types of liquid fuel furnaces placed on the market, we will refer only to the "Ferguson" furnace, which answers the demands of practice well, both as to regularity and uniformity of heating and economy of operation.

In the Ferguson furnaces air is blown, under a pressure of between 35 and 40 cm. of water, in two jets; the first and principal one carries the hydrocarbon, dropping from an automatically regulated valve, into a vertical chamber in which there is partial combustion of part of the hydrocarbon and complete

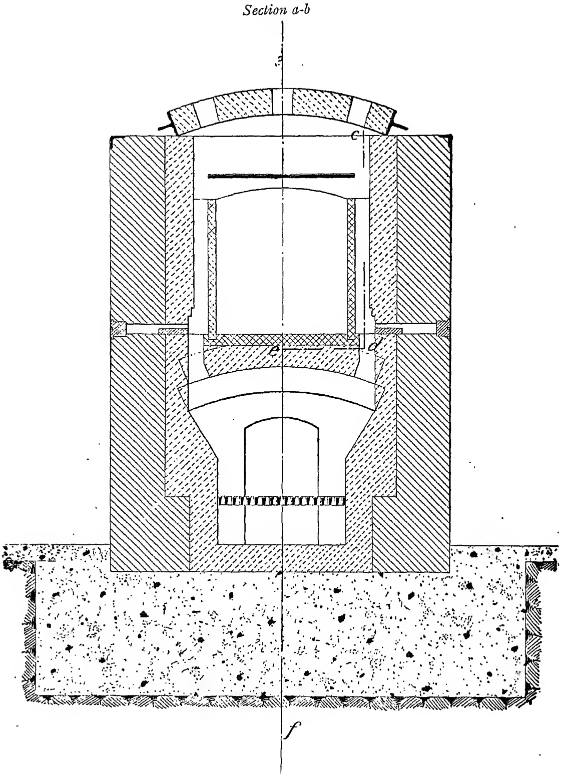

FIG. 86.

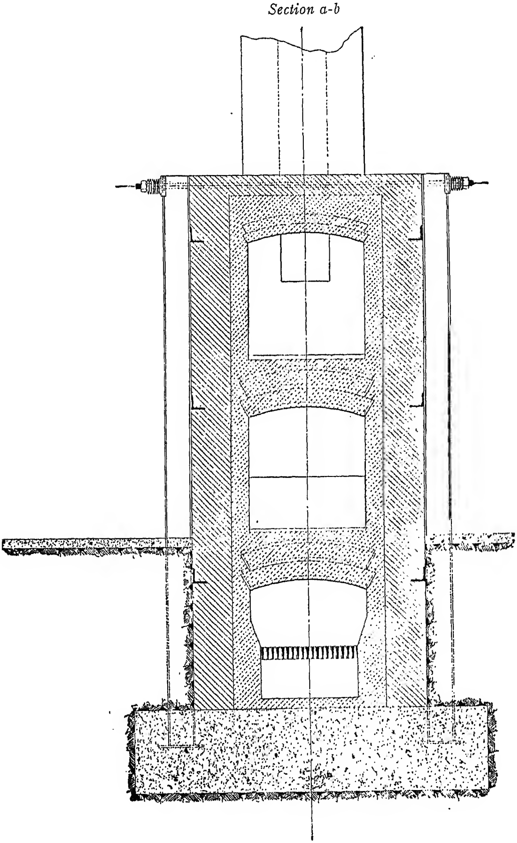

FIG. 87.

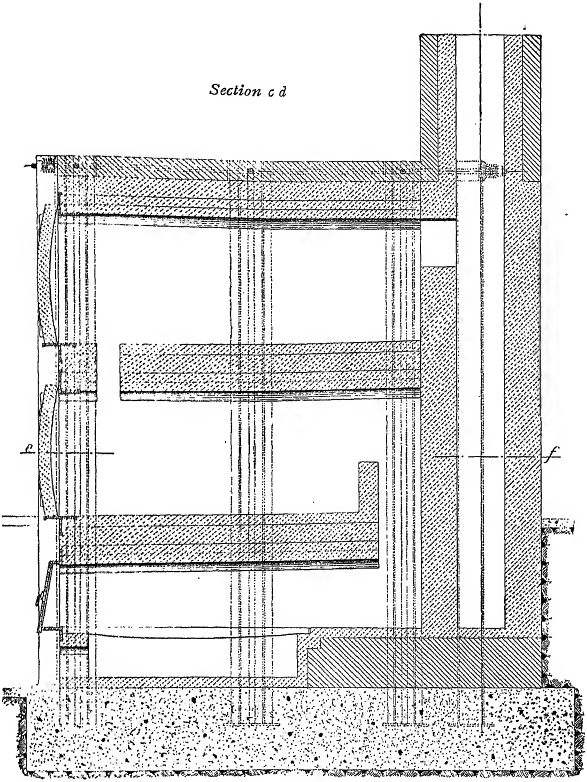

FIG. 88.

Section e-f

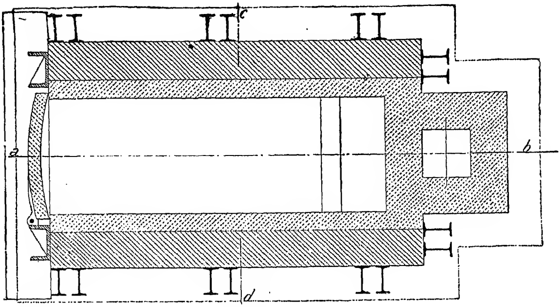

FIG. 89.

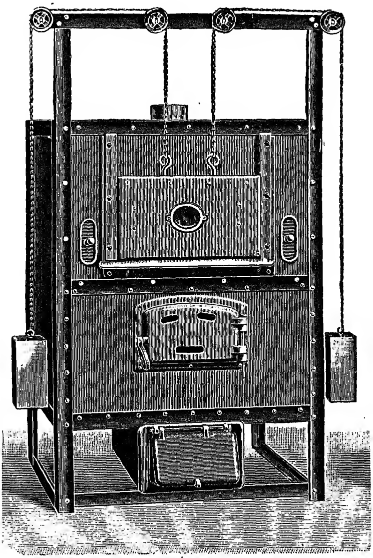

FIG. 90.

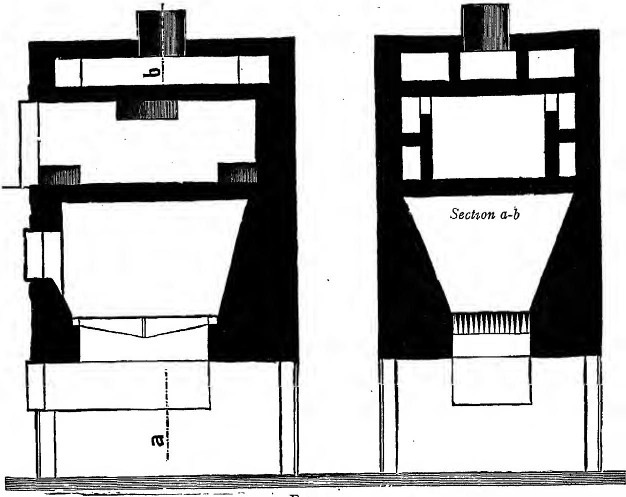

FIG. 91.

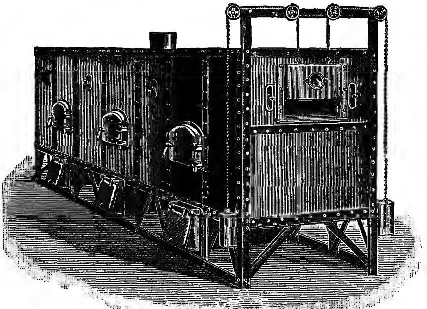

FIG. 92.

volatilization of the remainder. In the upper part of the chamber the vapor of the hydrocarbon meets the second and minor jet of air, with which it mixes intimately and burns completely.

The hydrocarbon oil must come to the furnace under a pressure between 500 and 1000 grams per sq. cm. (7 to 15 lb. per sq. in.).

The principal advantages of these furnaces are the following:

1. Great ease in obtaining in the laboratory of the furnace a neutral or reducing atmosphere; this greatly increases the life of the cementation boxes.

2. Ease and rapidity in starting.

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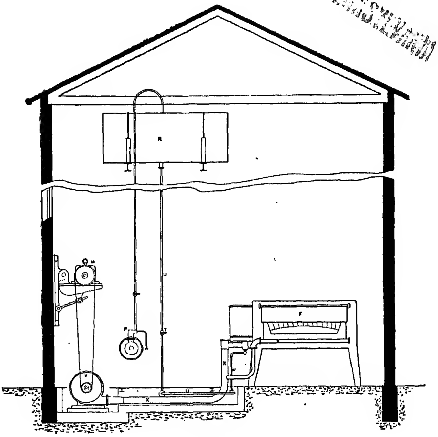

Fig. 93.

3. Ease and certainty in regulating the temperature, which can be kept satisfactorily constant within very wide limits; in general, at any point between 700° C. and 1400° C.

4. Marked economy in operation, due to the fact that fuels of the lowest commercial value (crude petroleum, heavy oils, coal-tar oil, etc.) can be completely consumed, utilizing their full calorific power.

Fig. 93 represents schematically one of the most convenient arrangements for the setting up of one or more Ferguson furnaces. The centrifugal ventilator *V*, set in motion by the motor *M*, furnishes the necessary current of air under the desired pressure (35–40 cm. of water); in the drawing it is seen that the air supply X is divided to supply the two jets of air spoken of.

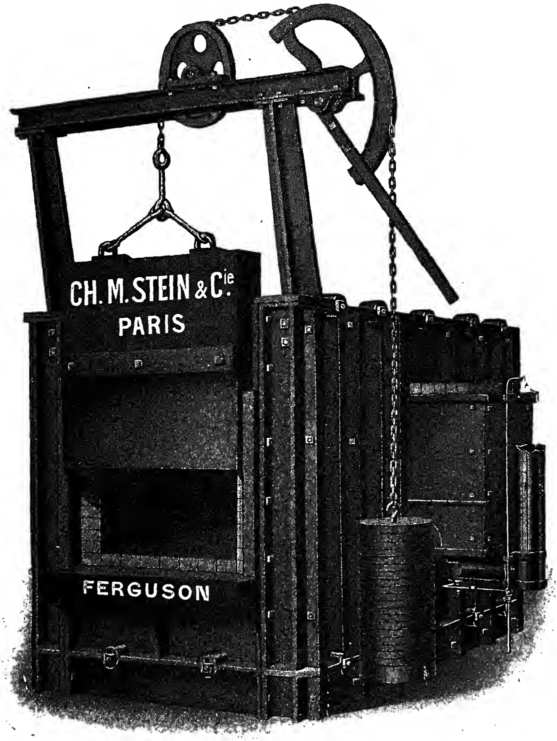

FIG. 94.

The hydrocarbon oil, contained in the reservoir R, reaches the furnace F through the tube U. The pump P serves to fill the reservoir R.

The Ferguson furnaces are constructed in a large number of shapes and sizes, according to the use for which they are intended. Fig. 94 represents one of the types which is best adapted to cementation in boxes, using solid cements. The furnace shown in Fig. 95 contains, besides the chamber intended for the heating of the cementation boxes, two other chambers adapted for the annealing and quenching of cemented pieces.

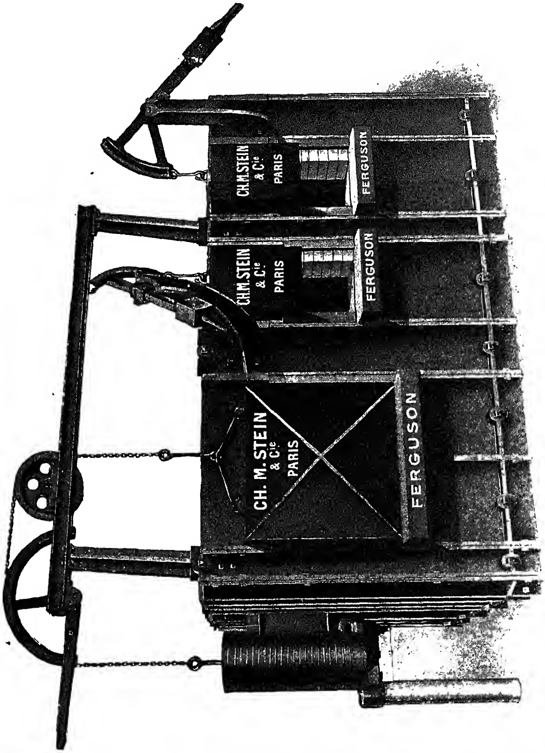

Fig. 95.

The gaseous fuel furnaces most frequently used for cementation are divided into two distinct types. To the first belong those heated by illuminating gas; their principal advantages consist in low cost and ease and rapidity with which they can be lighted and started without any special preliminary heating. These characteristics render the illuminating gas furnaces especially adapted to small plants operating intermittently.

Furnaces heated with producer gas, the second type or class, while they present marked advantages, compared with illuminating gas furnaces, especially in economy, regularity and constancy of operation, are more expensive to instal, are more cumbersome, and, on account of their bulk and that of the heat recuperators necessary to obtain sufficiently high temperatures, require a long time and a careful preliminary heating to be lighted and put in operation. They are adapted, therefore, only to continuous operation.

Among the innumerable varieties of gas furnaces of the two types at present on the market, we will describe only those which are best adapted to cementation practise.

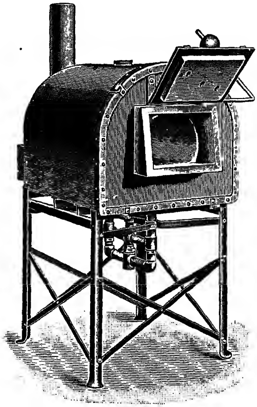

Fig. 96.

Among the cementation furnaces of small and medium dimensions heated with illuminating gas the muffle furnaces constructed by the firm of Wilhelm Hertsch of Stuttgart are very economical. Fig. 96 represents one of these furnaces. For a muffle 400 mm. wide by 240 high and 600 deep, the complete furnace costs 920 marks ($225). It requires air under a pressure of about 35 cm. of water, consumes about 7 cu. m. (250 cu. ft.) of gas per hour, and reaches a maximum temperature of about 1300° C. in less than thirty minutes.

A furnace similar to that just mentioned, but working without air under pressure, is the muffle furnace of Fletcher, Russell and Co., of Warrington, England, shown in section in Fig. 97 and in perspective in Fig. 98. This furnace is well adapted to the cementation of small pieces. It is, however, not very economical as to consumption of fuel; this follows of necessity from the fact that the gases of combustion remain in contact with the charge or laboratory walls for quite a short space, and issue from the furnace at a high temperature.

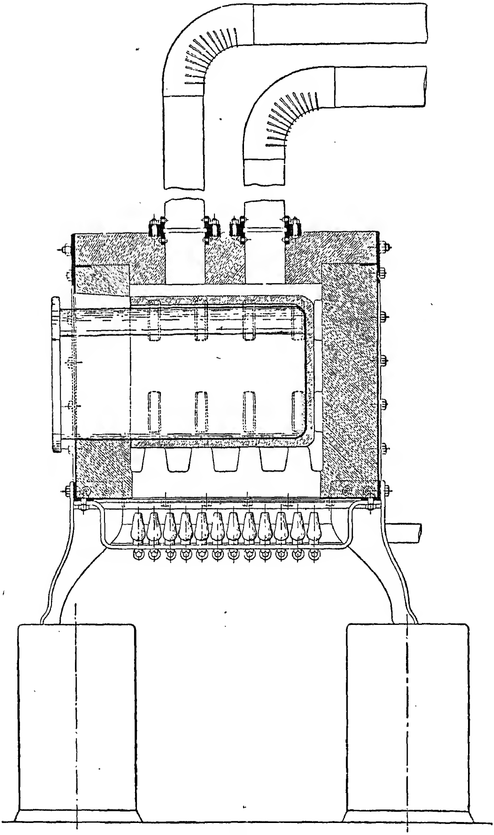

FIG. 97.

The greater part of the muffle cementation furnaces heated by illuminating gas, as they exist on the market, do not differ fundamentally from this one, and it does not seem necessary, therefore, to describe others. The use of muffles of refractory material has the great advantage of protecting the cementation boxes from direct contact with the flames, an action which becomes exceedingly harmful, decreasing greatly the life of the boxes, whenever a neutral or reducing atmosphere can not be obtained and maintained with certainty in the laboratory of the furnace. This happens in the great majority of cases.

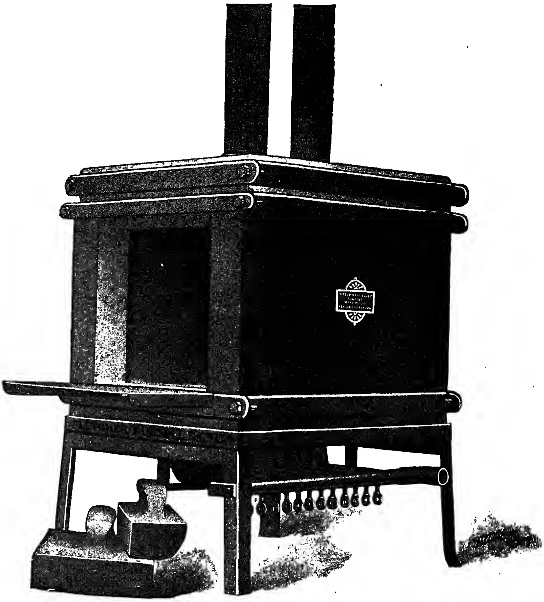

FIG. 98.

On the other hand, however, the muffles of refractory material can be made in practice only of relatively small dimensions and even for such dimensions their fragility makes their life quite short and therefore the cost very high, especially when rather heavy cementation boxes are charged in them.

Moreover, the utilization of the heat generated by the fuel is made considerably less perfect by the interposition of the refractory wall of the muffle, which is not only a cause of greater consumption of fuel but aggravates all the disadvantages which are due to slowness of heating of the boxes. The disadvantages just cited diminish when the muffles of refractory material are replaced by muffles of cast iron or cast steel, which are stronger and better

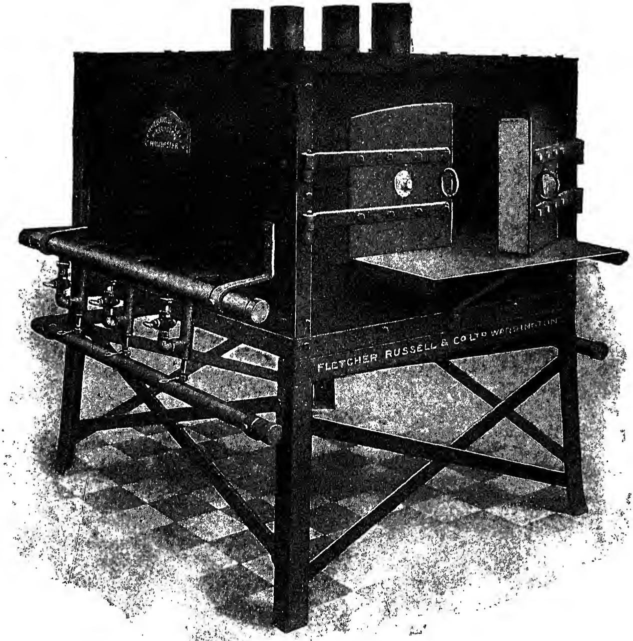

FIG. 99.

conductors of heat than those of refractory clay. However, such can be used only at relatively low temperatures (about 900°), for at higher temperatures they "swell" and may easily melt locally on the least overheating. Those of cast steel also cost too much; both are easily oxidized when they come in direct contact with the flames, so that their use merely lays upon the muffle disadvantages which would be averted from the boxes.

To avoid the disadvantages of muffles, hearth furnaces are built in which the cementation boxes, carefully closed, are placed directly in the combustion chamber, and the flames are so directed as to bathe as much as possible the walls and the arch of this chamber, without directly enveloping the cementation boxes. The heating of the latter is effected, therefore, more by the heat radiated from the walls and arch of the laboratory than by the heat communicated directly to the boxes by the flames. Furnaces of the type just referred to, heated by coal gas, are made in an exceedingly great variety of forms and sizes by many firms.

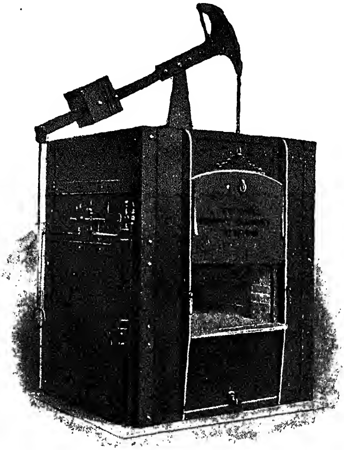

FIG. 100.

Fig. 99 represents one of these furnaces, made by the house of Fletcher, Russell and Co., of Warrington. The available space in the chamber is

60 cm. wide by 30 cm. high and 90 cm. deep. As is seen from the illustration, the flames enter the heating chamber near the hearth.

Analogous to these but heated *from above* are the furnaces constructed by the "Rockwell Furnace Company" of New York. Fig. 100 is the exterior view of one of these furnaces, especially adapted to cementation in boxes. Figs. 101, 102, and 103 show how the heating is effected from above. The same furnace can be used for burning heavy oils "vaporized" by means of one of the well-known vaporizers. The heating from above, obtained in the way indicated in the accompanying figures, seems in fact to assure the obtaining of a gradual, more uniform and more constant heating of the objects placed in the chamber than can be obtained by heating from below.

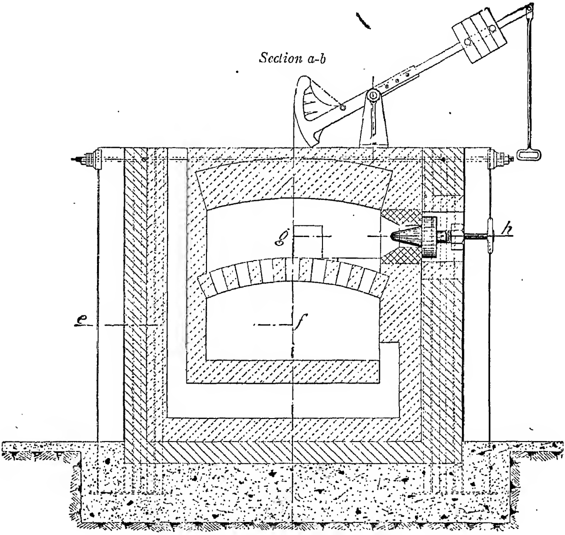

FIG. 101.

Furnaces heated from above, such as the type just described, present the disadvantages of higher cost of equipment and greater difficulty and cost of repairs of the refractory parts; disadvantages not wholly compensated by a somewhat lower consumption of fuel than in furnaces heated from below.

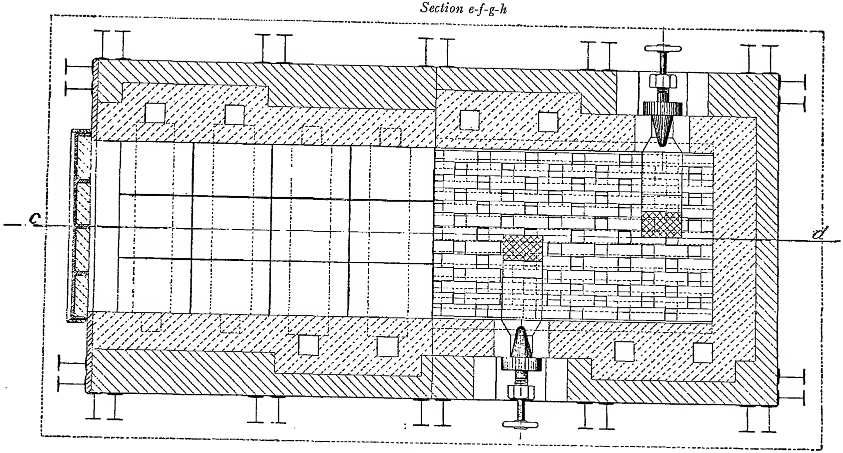

FIG. 102.

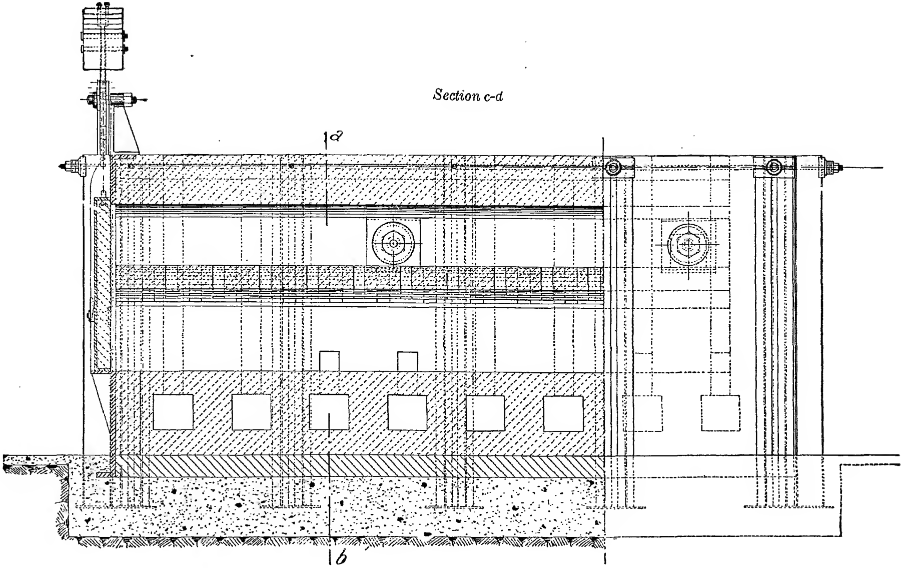

FIG. 103.

To partially eliminate the disadvantages of each of the two types of furnaces, the same Rockwell firm makes a special type of furnace which can be heated by illuminating gas or heavy oil, in which the circulation of the gases is effected as shown in Figs. 104 and 105. The combustion of the gas or hydrocarbon vapors is effected in the chamber below the laboratory of the furnace; the hot gases circulate in appropriate channels around the laboratory, enter it from above and issue at the bottom, near the end opposite to that at which they entered. This furnace costs less than that heated from above, and its up-keep is considerably easier and less costly. The uniformity and constancy of temperature in the various parts of the laboratory, although not equal to those obtained with furnaces heated from above, are amply sufficient for the greater part of practical cases.

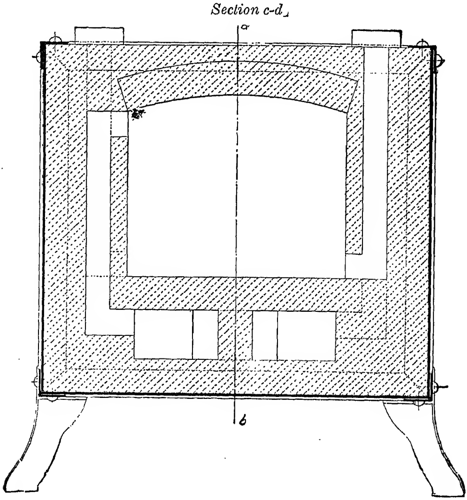

FIG. 104.

When a supply of illuminating gas is not available, the gas furnaces described in the preceding pages may be run by gasoline gas, obtained from one of the usual air-current vaporizers. It is well known, however, that the gas thus obtained is very expensive; moreover, the operation of the various apparatus required is not free from danger

Besides the normal types of illuminating gas furnaces referred to in the preceding pages and intended to heat ordinary rectangular cementation boxes, there are on the market gas furnaces of various forms designed for the cementation of pieces of special forms which can not be placed in the usual boxes. As an example of these there is a vertical cylindrical furnace intended for the cementation of very long pieces (as, for example, the axles of railway cars), constructed by the "Società Italiana per la Cementazione e gli Acciai Speciali" of Turin, shown in Fig. 106. This furnace is heated throughout its whole height by a series of independently regulated burners, fed with illuminating gas and with air under pressure (about 70 cm. of water).

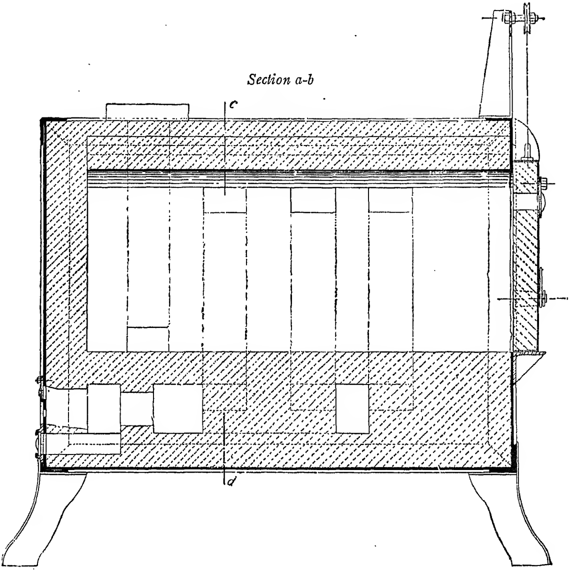

Fig. 105.

The stopcocks which furnish gas to each of the two series of burners are first regulated so as to obtain approximately the same temperature in the two parts of the furnace. By regulating then, with care, the width of the two exits for the products of combustion, at the upper and the lower part of the furnace, it is easy to obtain complete uniformity in temperature throughout the whole length of the laboratory of the furnace. A tube of wrought steel forms the cementation box. The axle to be cemented is placed in this tube and surrounded by the solid or mixed cement. The tube is then placed upright inside the furnace.

We will now show some examples of producer-gas furnaces chosen from those which I find to have given the best results.

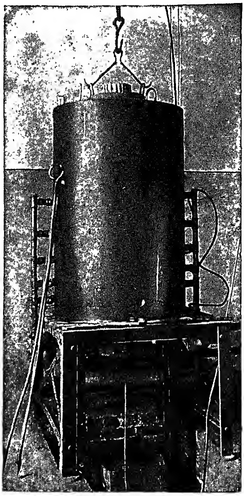

FIG. 106.

Fig. 107 shows a longitudinal section of a furnace heated by producer gas, constructed by Ch. M. Stein of Paris, and intended to cement simultaneously pieces of steel of ordinary forms and dimensions in cementation boxes, as well as pieces of large dimensions, such as connecting rods, shafts, axles, etc. Fig. 108 is a transverse section of the same furnace along the line *AB* of the preceding figure.

The flues for the entrance of the gas (6) open into the flues for the entrance of the air (8), which the air reaches by the horizontal channels (7); combustion of the mixture of gas and air is effected in (5), and the products of combustion, after having heated the walls and arch of the laboratory of the furnace, issue through the channels (9), from which they return into the passage (10), thence into the principal flue (not shown in the cut), and finally escape.

Opposite the door in the middle of the laboratory of the furnace are placed cylindrical crucibles (11), which occupy the whole height of the laboratory and pass through the arch of the furnace. The front half of the laboratory is intended for the heating of the ordinary cementation boxes (13) lying on balls placed on special tracks (14) set in the hearth. A series of dampers placed along the channels (6), (7) and)10), regulate the gas and air which reach the furnace and the draft of the chimney.

The boxes (13) are put into the furnace through the openings (15), which are then closed by means of doors (16); these details are represented in Figs. 109 and 110. The door is suspended by a chain to a beam (22) with counterpoise (23), and is formed of a steel frame in which, held by the wedge

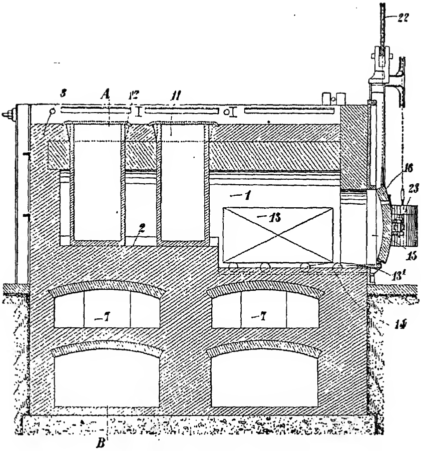

FIG. 107.

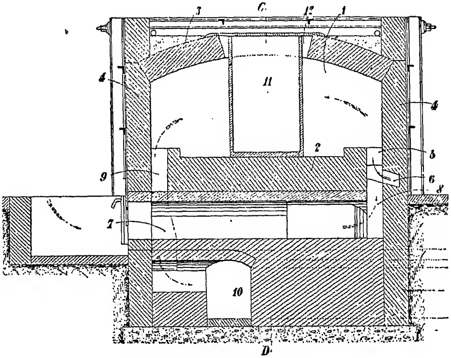

FIG. 108.

(19) provided with bolts (20), are placed refractory bricks forming the wall, pierced by holes (21) designed to allow of pyrometric measurements inside the laboratory. When the door is placed in front of the opening (15), a system of levers and eccentrics, shown in Figs. 109 and 110, permits of tightly pressing it against the well-planed walls of the furnace (by means of a simple turn of the axle 25, controlled by a key), so as to obtain tight closing without recourse to luting with clay.

Pieces of elongated form and of large dimensions which are to be cemented (or annealed or tempered) at the ends are placed with the ends to be cemented in the crucibles (11), suspending them from above to a cross-piece not shown in the figure. Two long cylindrical pieces placed in this way are to be seen over the furnace, to the left, in Fig. 111, which shows the exterior of two coupled furnaces of the type just described.

The crucibles (11), after the pieces to be treated have been placed in them in the manner indicated, are filled with the solid cement (or with inert substance, such as refractory earth, if it is simply a question of annealing or hardening), covered with pieces of sheet iron and then carefully luted with refractory earth.

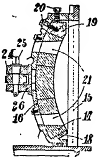

FIG. 109.

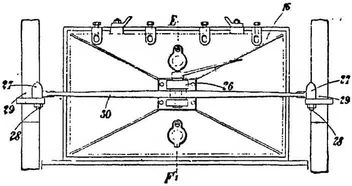

FIG. 110.

The gas necessary for the heating of the furnace is furnished by a producer, which may be independent of or constructed in the mass of the furnace itself. A furnace of this type has been in operation for a long time in the works of the "Fives-Lille" Society at Fives, and gives very satisfactory results, especially since it permits of cementing and hardening the ends of long pieces such as connecting rods and locomotive shafts, avoiding the deformation which always occurs when such pieces are heated all over for a long time (for cementation or for quenching) in a horizontal position. When long pieces are not to be cemented, the same furnace can be used entirely as an ordinary furnace by merely doing away with the crucibles and utilizing the whole laboratory for the heating of cementation boxes.

This is the type of furnace at present adopted by most of the automobile factories. A good example of this is the equipment furnished by Stein for the Renault automobile factory at Billancourt. Fig. 112 shows the arrangement

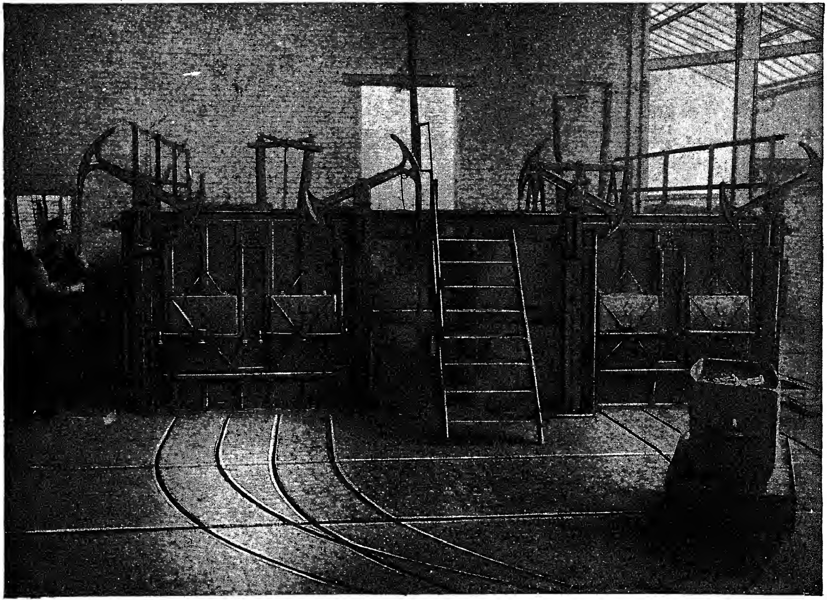

Fig. 111.

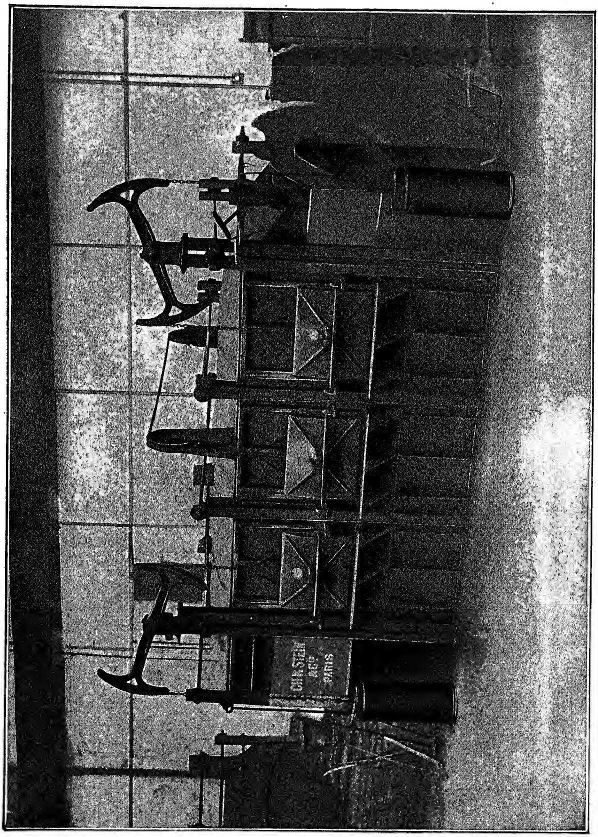

FIG. 112.

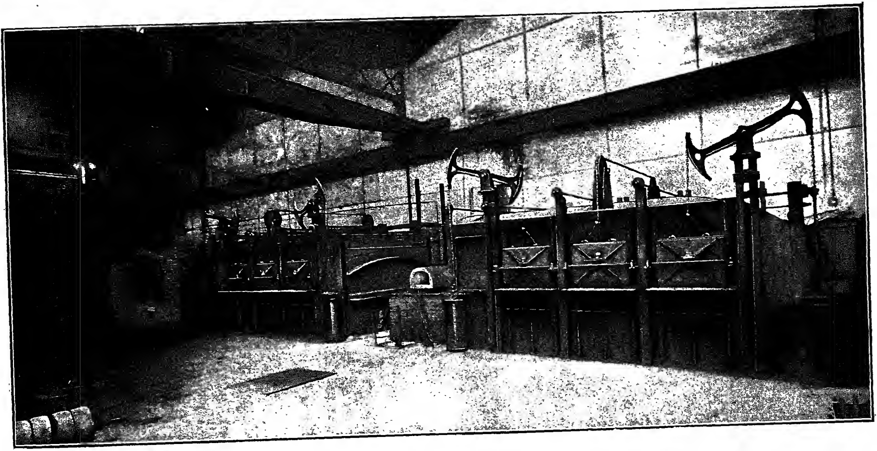

FIG. 113.

of one of these furnaces. The equipment (Fig. 113) comprises two furnaces, each having an available hearth surface of 2.50 × 3 meters; the gas is supplied by a battery of independent producers using gas works coke, and reaches the furnace through underground flues. The two furnaces can be operated separately, but like all furnaces of this type, they must operate continuously. They can easily be placed under reduced operation by means of manipulating a few dampers; when these are adjusted they can be left completely alone as long as thirty-six hours.

The temperature of the laboratory can easily be regulated so as to keep it constantly within a variation of about 10° C.; the differences in temperature between different points in the laboratory do not exceed 10° C. when the temperature lies between 800° and 1100° C.

The perfect closing of the doors is insured by a lever and eccentrics such as already described for the furnace with vertical crucibles, and there is no need of luting.

The pressure of the gases in the furnace is a little higher than the external atmospheric pressure, and it is easy to obtain at will an oxidizing or reducing atmosphere.

The uniformity of temperature of the furnace is due essentially to the fact that the heating of the boxes placed in it is effected solely by the heat radiated by the arch heated by the flames, and by the heat transmitted through the hearth, under which these flames circulate.

We will add some considerations on the solid cements which practice has shown to be best adapted to obtaining particular results in case-hardening. Without stopping to discuss the innumerable cementation powders proposed by many inventors and protected by numerous patents, we will describe the preparation, use and effects of those solid cements which long experience has shown to be most effective and best adapted to furnishing definite results.

Many manufacturers, some of undoubted standing, put on the market cementation powders already prepared, the composition of which they keep secret and of the efficacy of which they give most marvellous guarantees. It is strange that purchasers can still be found to-day disposed to pay high prices for such mysterious powders, when with a little trouble they could acquire the fundamental knowledge of the laws governing cementation and thus prepare for themselves, at much smaller cost, perfectly satisfactory carburizing mixtures and work out the methods for any designed purpose.

In general, the manufacturers of cementation powders limit themselves to classifying their products in two general groups: the "rapid cements" and the "slow cements." The consumer who has only these indications can not solve the innumerable delicate practical problems in cementation which present themselves every day, especially considering the wide introduction and use of special steels, such as nickel, chromium, chromium-nickel, tungsten, vanadium steels, etc.

There are only some *types* of *simple* cements, at present well known, whose efficacy is a *maximum* from all points of view, and the addition of other ingredients to these typical cements *in no wise increases their efficacy.* Such additions rob them of their principal merit—purity, which guarantees the purity of the product, and simplicity, which determines with precision their mode of acting and the conditions best suited for obtaining a definite result.

These last considerations hold especially for gaseous cements and mixed cements, but they have a real practical value also in the case of solid cements.

The simplest among the solid cements is more or less finely divided carbon. Of the carbons of different varieties usually employed for the preparation of solid cements, the purest is wood charcoal. However, simple powdered wood charcoal used for short cementations to produce thin cemented zones (from 0.5 mm. to 1 mm. thick) presents the disadvantage of furnishing too low and irregular carbon content. This phenomenon was explained fully on p. 184, where it was shown that the carburizing activity of pure wood charcoal, almost entirely free from volatile organic substances, is due only to the carbon monoxide formed by the action of the oxygen of the air occluded in the carbon. But low carbon content in the cemented zones results when carbon monoxide acting in the presence of carbon is diluted with nitrogen, as has been already explained. The strong irregularities of these zones are due to the fact that in the mass of the carbon the most finely powdered parts accumulate against some sections of the surface of the steel to be cemented, rendering the access of the carburizing gases difficult. The same low carbon content of the cemented zones which are obtained with wood charcoal, while it constitutes a disadvantage for thin cemented zones, may be advantageous in deeper cementations, in which the cements of more "intense" action have the serious defect of furnishing cemented zones in which the maximum carbon content is too high. This is the reason why many manufacturers of armor plates have abandoned the use of hydrocarbons or of the more rapid solid cements (for example, the mixtures of carbon and of barium carbonate) to return to the use of simple pure wood charcoal, which, although requiring a much longer time to furnish cementation of a given depth, guarantees against the reaching of too high carbon contents in the cemented zones.

Other forms of less pure carbon are preferable for case hardening. The presence in these of not wholly decomposed organic residues or of large proportions of ashes rich in alkali or alkaline earth carbonates, gives rise to the formation of gases (hydrocarbons, cyanides and carbon dioxide, respectively), whose action, in the presence of free carbon, produces an increase in the maximum carbon content in the cemented zones. Among these varieties of carbon most frequently used for surface cementation are bone charcoal, leather scraps, residues of incompletely carbonized hoofs or horns, lamp black, etc. In any case, these substances must be pulverized and well dried before using.

Many manufacturers are accustomed to mix the different varieties of carbon, in definite proportions, which permits, in a certain way, of "graduating" (although only with a very rough approximation) the "intensity" of the carburizing action of the cement in such a way as to make it higher than the minimum value which it has for simple wood charcoal but lower than the excessive values which it reaches for the other varieties of carbon mentioned above.

It may be said that every manufacturer uses mixtures of special composition, which, moreover, all give good results, for each manufacturer has had to determine, by means of long-repeated trials, the special conditions under which the mixture used by him must be made to act.

Among these mixtures I shall cite, as examples, the following:

(*A*)	Powdered oak charcoal	5 parts
	Powdered leather charcoal	2 parts
	Lamp black	3 parts
(*B*)	Powdered beech charcoal	3 parts
	Powdered horn charcoal	2 parts
	Powdered animal charcoal	2 parts

Mixtures are frequently used of various kinds of carbon with organic substances (such as horn scrapings, flour, beer dregs, resin, glue, heavy mineral oils, etc.) or mineral salts (especially alkali and alkaline earth carbonates, alkalis, cyanides, ferrocyanides, common salt, etc.). It is easy to understand the action exercised by organic substances easily decomposed by the action of heat, or by those salts which evolve carbon dioxide at a high temperature, or by cyanogen or its derivatives (nitrogenous organic substances, alkali cyanides, ferrocyanides, etc.).[1] The effect of other substances which many manufacturers add to their cement is, on the contrary, not easily explainable; such, for example, are glass, siliceous sand, kitchen salt, etc.

It must be pointed out at once, however, that recent experiments show that the efficacy of these substances is small and sometimes null.

A simple mixture recommended by various authors and used by many manufacturers is:

(C)	Wood charcoal	90 parts
	Sodium chloride	10 parts

It seems that this cement, used in many machine shops, gives better results than simple wood charcoal. For this it is not easy to give a scientific reason. It is, however, certainly less efficacious than the cement of the following composition:

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[1] We have already seen (p. xiii) that the use of cyanide compounds was proposed as early as the beginning of the nineteenth century by the American professor, A. K. Eaton.

(*D*)	Powdered wood charcoal	60 parts
	Barium carbonate	40 parts

This is one of the best solid cements, both because we know well its mode of action, which I have already shown (see p. 184) is due to the simultaneous activity of the wood charcoal and of the carbon monoxide formed by the action of this carbon on the barium carbonate, and because for cementations of small depths it gives cemented zones markedly more homogeneous than those furnished by the other solid cements. In general, the maximum concentration of the carbon in the cemented zones obtained with carbon and barium carbonate at temperatures between 900° and 1100° C. varies from a minimum of about 0.7%, for the very thin zones obtained near 900°, to a maximum of about 1.3% for the zones thicker than 1 mm. obtained near 1100° C.

Another advantage of this cement lies in its property of being "regenerated" easily and spontaneously when it is left exposed in a thin layer to the air, after having used it in the usual manner. This process of "regeneration" is due to the fact that the barium oxide formed during the cementation, by the dissociation of the barium carbonate, absorbs carbon dioxide from the air, again forming barium carbonate.

After a certain number of alternating cementations and regenerations it is necessary to add some wood charcoal to the cement to replace that burned during the cementation and during the discharging of the boxes.

The preparation of this cement consists simply in finely grinding and intimately mixing the wood charcoal and barium carbonate.

The barium carbonate is found on the market sufficiently pure at about 50 centesimi (10 cents) per kilogram. If natural barium carbonate (*witherite*) is used, it is necessary to powder it carefully before adding it to the carbon; the finely divided precipitated barium carbonate, on the contrary, can be mixed directly with the granulated carbon and the one operation of grinding the carbon can be used for preparing the mixture.

On varying the proportions of the two components, the results which are obtained vary, working under definite conditions. It is difficult to establish rules predicting the direction and the importance of these variations, because the action of this cement[1] depends to a great extent on the rate at which the temperature rises in the various parts of the cementation boxes;

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[1] In reality, this cement acts as a "mixed" solid-gaseous cement, but in the practical definition of a cement we must take into account essentially the substances which we can regulate directly and whose action we can govern; now, this is certainly not the case for the carbon dioxide which is evolved from the barium carbonate of this cement. We can regulate only the carbon and the barium carbonate.

in fact, this velocity determines the extent and the rapidity of the evolution of carbon dioxide in the various phases of the cementation.

The differences in the course of the cementation to which variations in the proportions of the carbon and barium carbonate may give rise are shown by some experimental results obtained by Guillet[1] by cementing for eight hours at 1000° C. with mixtures of wood charcoal and barium carbonate in varying proportions an ordinary dead soft steel with 0.05% of carbon, and then analyzing successive layers 0.25 mm. thick:

Compositon of the Cement		Concentration of the Carbon	
Wood charcoal, parts	Barium carbonate, parts	In 1st layer, percent.	In 2nd layer, percent.
80	20	1.14	0.75
60	40	1.32	1.19
40	60	0.94	0.77

Both this cement and those consisting of various qualities of carbon, pure or mixed with each other, or with sodium chloride present the disadvantage of low thermal conductivity, which, as already explained, aggravates the most important disadvantages of using solid cements in boxes. Some other cements, still with carbon as base but containing other salts or organic substances, do not possess this particular disadvantage of low heat conductivity, but are in other respects inferior to the carbon and barium carbonate cement.

(*E*) Coke saturated with heavy mineral oils.

This is a very "quick" cement, in the sense that it gives rise in a short interval of time (two to three hours) to thin cemented zones of very high carbon content, from 1.5 up to 1.8% according to the temperature. It is very rapidly "exhausted," however, and is not suited for prolonged cementations intended to give cemented zones deeper than a few tenths of a millimeter.

Moreover, even in the case of very thin cementations, such "quick" cements can be usefully employed only when the cemented and hardened pieces are intended to resist friction only, but not shocks; because in their zones of high carbon content and of sudden variations in the carbon concentration shocks would rapidly produce fracture and exfoliation, as explained in the first part of this volume.

Besides, this cement presents another serious disadvantage, of not behaving in a constant and uniform manner when the conditions under which cementation is effected are kept as constant as is attainable in practice. In other words, in using this cement it is not possible to regulate the conditions of the operation in such a way as to obtain well-defined predetermined results.

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[1] *Mém. de la Société des Ingénieurs Civils de France*, 1904, p. 189.

Three other cements, recommended by Grenet and which have given good results in practical tests, are the following:

(*F*)	Powdered wood charcoal	1.0 kg.
	Salt	0.1 kg.
	Sawdust	1.5 kg.
(*G*)	Coal with 30% of volatile materials	0.5 kg.
	Charred leather	0.5 kg.
	Salt	0.1 kg.
	Sawdust	1.5 kg.
(*H*)	Charred leather	1.0 kg.
	Yellow prussiate	0.2 kg.
	Sawdust	1.0 kg.

The velocity of cementation increases gradually from the first to the third of these cements.

The efficacy of the sawdust, which renders the mass porous and easily penetrable by the gases, is easily explained by the increased activity of the gases.

There are also used as cements some pure carburizing salts or mixtures of various salts, such as potassium ferrocyanide, or the mixture of two parts of potassium ferrocyanide with one part of potassium bichromate. These are very "quick" cements, and are used almost exclusively for very thin cementations (about a tenth of a millimeter); in this case they are not used in boxes but by spreading as a varnish on the objects to be cemented. In cementations carried out in this way, the cement always undergoes more or less complete fusion, and then behaves like a liquid cement. With these processes I shall deal later, in speaking of liquid cements.

As I have already said, there are in use in machine shops numerous mixtures of the most varied and complex composition. The results of accurate and precise experiments do not justify, however, the use of such complex mixtures, which do not furnish results superior to those which are obtained with the less complicated cements, and, further, because of their complexity, do not furnish results which are constant or uniform and can be exactly predicted. The best and surest results are always obtained by using the simplest cements.

One of the most serious disadvantages of solid cements, simple or complex, lies in the impossibility of determining *a priori* with certainty the results which will be obtained by cementing under definite conditions a steel of definite composition.

This is due especially to the impossibility of knowing with precision the velocity with which, in the various cements and under the various conditions, the propagation of heat takes place through the charge from the outside to the interior of the charges contained in the cementation boxes. This is well known to every one who has had experience with surface cementation, and is proved by a simple comparison of the experimental data reported by various authors. Some data of this kind, determined by Guillet, have been already reported in the form of diagrams in the first part of this volume (see p. 49). We copy here the exact values (depths of the cemented zones in tenths of a millimeter) obtained in these experiments of Guillet, in order to facilitate comparison with other data.

(*a*) Cementation of an ordinary soft cabron steel *eight hours* at different temperatures and with different cements.

Temperature	Composition of the cement			
	60 parts of carbon + 40 parts of barium carbonate	2 parts of potassium ferrocyanide + 1 part of potassium bichromate	Potassium ferrocyanide	Wood charcoal in fine powder
700° C.	0.0	0.0	0.0	0.0
800°	5.0	8.5	5.0	5.0
900°	22.5	17.5	20.0	12.5
1000°	35.0	32.5	32.5	25.0
1100°	45.0	45.0	50.0	35.0

(*b*) Cementation of same at 1000° C. during various times and with different cements:

Time (hours)	Composition of the cement					
	60 parts of carbon + 40 parts of barium carbonate	Ferrocyanide + bichromate	Unwashed animal charcoal	Wood charcoal		Carbon + potassium carbonate
				In fine powder	In coarse powder	
1	8	8.5	9.0	7.5	7.0	15
2	10	9.5	15.0	13.5	11.0	20
4	12	12.5	22.5	16.0	15.0	24
6	20	19.0	27.0	18.5	17.5	28
8	30	32.5	32.5	25.0	23.5	35

More recently[1] Guillet himself determined more precisely the data relative to the cement formed of forty parts of barium carbonate and sixty of carbon, reporting the following numbers:

Penetration desired (mm.)	Length of cementation at a temperature of 850° C.	Length of cementation at a temperature of 1000° C.
0.5	2 hours 30 minutes	0 hours 30 minutes
0.8	4	1
1.0	6	2
1.2	7	3
1.5	8	4
2.0	..	6
2.5	..	8

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[1] *Le Gênie Civil*, 2d sem., 1911, p. 228.

Guillet points out that to avoid serious mistakes it must be remembered that in the table reported above the length of the cementation is calculated from the moment at which the box is *externally* at the temperature 850° and 1000° C. Moreover, the numbers reported above hold for boxes of sheet iron in the form of cylinders 120 mm. in diameter, in which the objects to be cemented are placed coaxially and in such a way that around them there is a layer of cement 5 cm. thick.

As is seen, the numbers reported hold only for very special conditions and it is not possible to furnish for solid cements data of entirely general character.

The results obtained with a given solid cement vary within wide limits even with small variations in the conditions of working: for example, with variations in the form and dimensions of the boxes and objects to be cemented; in the arrangement of these objects and cement in the boxes; in the construction and working of the furnace used, etc.

Thus, to cite only a few of the numerous examples which might be given, in a table reported by Lake[1] for cementation carried out with the usual cement of carbon and barium carbonate for eight hours at 900° C., we find a penetration of 2.75 mm. instead of the 2.25 mm. given by Guillet or the 2.20 mm. obtained by Shaw Scott,[2] or the 1.2 mm. obtained by Grayson[3] by cementing for seven hours at 950°–1000° C. Thus also, by cementing with charred leather at 900° C., while Grayson obtains in six hours a cemented zone of 0.035 inch, Lake, under the same conditions, obtains in four hours a zone of 0.062 inch; that is, almost double the value in two-thirds the time.

The differences between the results obtained by various experimenters in the cementation of special steels are still greater. Thus, for example, Guillet, cementing a steel with 2 percent. of chromium under conditions where an ordinary carbon steel would have given a cemented zone 0.9 mm. thick, obtains a cemented zone 1.1 mm. thick, while Giesen,[4] to obtain about the same penetration (1.2 mm.) with the same 2% chromium steel, protracts the cementation for ten hours at 1100°, using the mixture of carbon and barium carbonate. Under the same conditions Guillet obtained, with a carbon steel, a penetration of 4.5 mm. in only *eight hours!*

Many of the wide divergences between data of this kind reported by the various authors must without doubt be attributed to the different (and often absolutely inexact) ways of estimating the depth of the cemented zones. It is not possible, however, to carry out a cementation with a solid cement, charging the boxes cold as usual, in such a way as to be sure to obtain cemented zones of a definite depth and with a given maximum carbon content.

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[1] E. F. Lake, *Composition and Heat Treatment of Steel* (New York, 1911, p. 235).

[2] *The Journal of the Iron and Steel Institute*, 1907, III, p. 126.

[3] *The Journal of the Iron and Steel Institute*, 1910, I, p. 298.

[4] Walter Giesen, *Die Spezialstähle in Theorie und Praxis*, p. 20.

The course of the cementation *under the average conditions which present themselves in practice*, when ordinary soft steels are cemented with the cement formed of 60 parts of wood charcoal and 40 of barium carbonate, is seen in a diagram (Fig. 114) due to Guillet,[1] which gives (in tenths of a mm.) the penetration of the carbon in successive hours when the cementation is conducted at a constant temperature of 850° C. and the steel subjected to the cementation contains 0.12% of carbon. The following diagram (see Fig. 115), along similar lines, is due to Shaw Scott.[2]

Scott's three curves indicate in mm. the penetration of the carbon in successive hours, when cementing ordinary soft steel at 900° C. with three different solid cements:

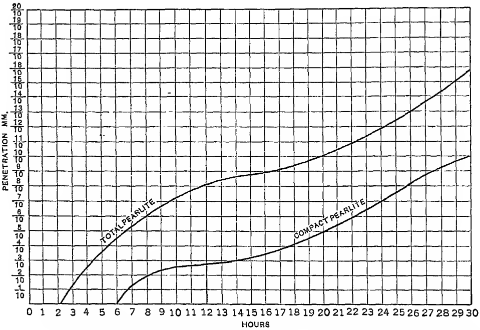

Fig. 114.—Curves of the penetration of the carbon at a temperature of 850° C. into a steel with 0.12 percent of carbon.

1. Carbon cement (40 parts of barium carbonate and 60 of wood charcoal (highest curve);
2. Carbonized leather (intermediate curve);
3. Wood charcoal (lowest curve).

As regards the action of solid cements proper on various special steels, we have up to the present few experimental data. Even these few data are not very reliable, or, at least, can not serve as guides in the various cases arising in practice, since they hold only when the cementation is conducted in a manner absolutely identical with that used for their determination.

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[1] See *Mém. de la Soc. des Ing. Civ. de France*, 1904, p. 192.

[2] *The Journal of the Iron and Steel Institute*, 1907, III, p. 127.

In the cementation of special steels with solid cements great variations in the characteristics of the cemented zones, due to very small differences in the conditions under which the cementation has been effected, are much more prominent than with plain carbon steels. In fact, outside of the few data given by Guillet, and already reported in the first part of this volume, the data given by other experimenters must be considered as lacking in any practical value whatsoever.

As an example of this, take the results of Giesen, in which any practitioner can point out large and evident errors. From his Table 7 (p. 19), it would follow that a steel with 0.5% of manganese, cemented for one hour at 850° C. with leather carbon, is carburized to a depth of 0.982 mm., while in the same steel, cemented for ten hours at 1100° C., the carburization reaches only 1.213 mm.! It must be noted, however, that Giesen determined the penetration of the carbon by weighing the specimens of steel before and after the cementation!

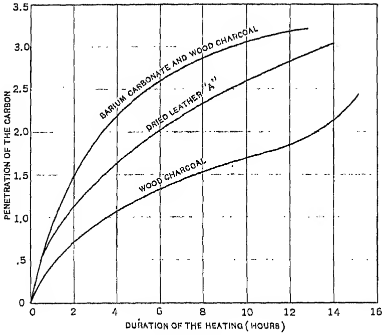

Fig. 115.

We have seen, and we shall see again, that the causes of error noted above do not show themselves at all, or to a much smaller extent, in cementation carried out with gaseous cements or with mixed cements.

Besides the velocity of the penetration of the carbon, another datum, of still greater practical importance, must be taken into account in judging of the quality of a cement and in the choice of the cement best adapted to a definite purpose; the maximum concentration and the distribution of the carbon in the cemented zones, as shown by the curves which we have called "cementation curves."

In cementation with gaseous cements or with certain mixed cements it is possible to choose the conditions of the cementation in sucl obtain with certainty cemented zones in which the concentrat bon does not exceed a definite value and varies from one layeı this zone in the most "gradual" manner, thus avoiding, or at lea reducing in extent, the phenomena of brittleness and exfo cemented and hardened zones. In cementation with solid ceı possible to even approximate results of this precision.

Under the action of "quick" solid cements the concent carbon rises rapidly in the external layers of the cemented zc comes more marked the greater the velocity with which the t cementation is reached and the higher this temperature. C group are advantageously used when it is necessary to ceme depth but to attain high carbon contents in the external lay mented zones, so as to obtain rapidly a very hard surface, and necessary to reduce their brittleness to a minimum. Such ar jected to friction but not to strong shocks, as, for example, gear engaged and carrying small loads.

The "mild" or "slow" solid cements give, by suitably ı cementation, very deep cemented zones without the concent carbon rising too high, even in the external layers of these cements are used with advantage whenever it is desired to ob zones of medium or great depth (for example, more than 1–2 n 25–30 mm.) and such as present, after hardening, minimum b minimum tendency to exfoliate.

Of the various solid cements mentioned in the preceding pa generally placed in the first group of "sudden" or "quick" which I have indicated by the letters (*A*), (*B*), (*E*), (*G*) and (*l* second group of "mild" or "gradual" cements those which I h by the letters (*C*), (*D*) and (*F*). But, from the point of view tration and distribution of the carbon in the cemented zone subdivision has no absolute value whatever, for the same cen according to the way in which the cementation is conducted, a cement or as a "gradual" cement.

Thus, for example, Caron's cement (60 parts carbon and 4 bonate) is a "gradual" cement when used at temperatures l and to cement objects of large dimensions (which heat up sl case it can furnish cemented zones more than 2 mm. th the concentration of the carbon does not exceed 0.9% surface layers. The same cement, on the contrary, becon when it is used at temperatures higher than 1100° C. to cem small dimensions; under these conditions it can furnish ceme which the maximum concentration of the carbon may

Analogous examples might be cited for the greater number of the solid cements.

It is clear, therefore, why the few present known "cementation curves" relative to the solid cements practically employed are very far from being as accurate as those for the gaseous cements and the mixed cements. Nevertheless, we will cite here some of the empirical data relative to some solid cements, in addition to those reported on p. 73.

Those published by Grayson[1] refer to cementation carried out in the usual boxes, on steel cylinders about 30 mm. in diameter and having the following composition:

Carbon	0.170 percent.
Manganese	0.704 percent.
Silicon	0.056 percent.
Sulphur	0.060 percent.
Phosphorus	0.047 percent.

The cements used were: 1. Ground bones. 2. A cement placed on the market under the name of "Brown Scintilla." 3. Ignited leather. 4. Caron's cement (60 wood charcoal and 40 barium carbonate), and called by the author "Hardenite." The following table contains the results of their analysis.

	Designations of the cement			
	Bone	"Brown scintilla"	Ignited leather	"Hardenite"
Carbon (fixed at 1000° C.)	8.0	11.0	69.0	44.0
Volatile matter and hydrocarbons.	26.5	53.0	15.2	14.1
Nitrogen	3.5	3.0	3.8	0.9
Ash	60.0	23.5	3.5	37.5
Sulphur	0.1	0.45	0.55	traces
Moisture	2.0	9.0	8.0	3.5
Total	100.1	99.95	100.05	100.0
	Analyses of the ash			
Phosphoric acid	16.0%	2.0%	0.10%	Traces
There were also present	Alumina Lime Ammonia	Alumina Lime Ammonia Soda Silica Carbonates	Alumina Lime Iron Silica	Barium Iron (traces) Silica Carbonates

The variations in the concentration of the carbon in the cemented zones were determined with great care by removing, on the lathe, from the cemented cylinders some thirty successive co-axial layers each about 0.0625 mm. thick and determining, by combustion and direct weighing, the carbon in each.

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[1] *The Journal of the Iron and Steel Institute*, 1910, I, pp. 287–302.

The results obtained at various temperatures and prolonging the cementations for different periods of time are collected in the four following diagrams, traced, as usual, by taking abscissas proportional to the distances of the analyzed layers from the external surface and ordinates proportional to the concentration of the carbon in the steel of these layers. The temperatures of cementation were determined simultaneously with a Féry pyrometer and a platinum resistance pyrometer. The author indicates only intervals of 50° C. between which the temperature remained during the whole cementation, but adds that the oscillations in the temperature never exceeded 30° C. This insufficient precision in the determination of the temperature and of its oscillations deprives Grayson's experiments of a great part of their practical importance, as results from our previous explanations.

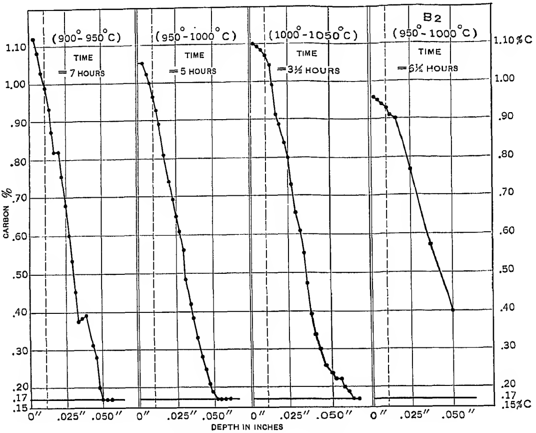

FIG. 116—Diagram 1. "Bone."

The first diagram (Fig. 116) contains the results of four cementations carried out with the first cement (bone) at the various temperatures indicated in the diagram. The fourth curve refers to a cementation carried out at 950°–1000° C. with cement already used for previous cementation at 950°. As is seen, the cement already used, and deprived therefore of the greater part of the volatile organic substances which it first contained, has become more "gradual," giving cemented zones of lower carbon content. This is an example of the fact, already stated, that cements containing volatile organic substances (hydrocarbons, etc.) are among the most "sudden" cements.

The second diagram (Fig. 117) contains the results of four cementations carried out with the second cement ("Brown Scintilla") at the various temperatures indicated in the diagram. As is seen, this is a case of a very "sudden" and very irregular cement. The four curves of the diagram offer a new confirmation of the irregularity and uncertainty of the results obtained with most of the solid cements in common use.

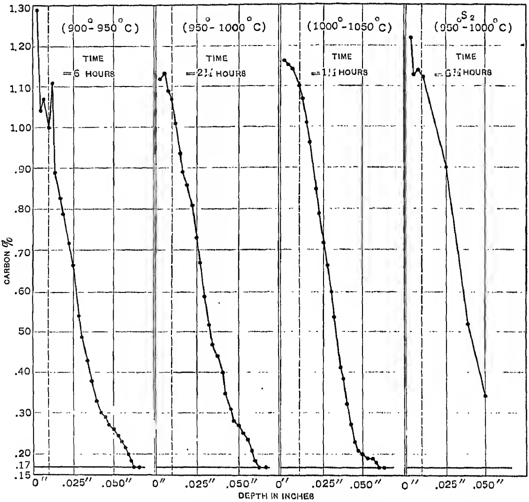

FIG. 117—Diagram 2. "Brown Scintilla."

The third diagram (Fig. 118) contains the results of four cementations with ignited leather. As is seen, this also is a very irregular but less "sudden" cement than the preceding. It is very easily exhausted, as follows from the fourth curve, which refers to cementation with cement previously used once.

Finally, the fourth diagram (Fig. 119) shows cementation curves ob-

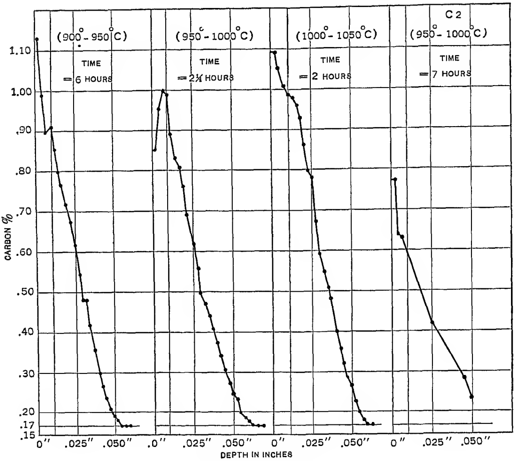

FIG. 118.—Diagram 3. "C."

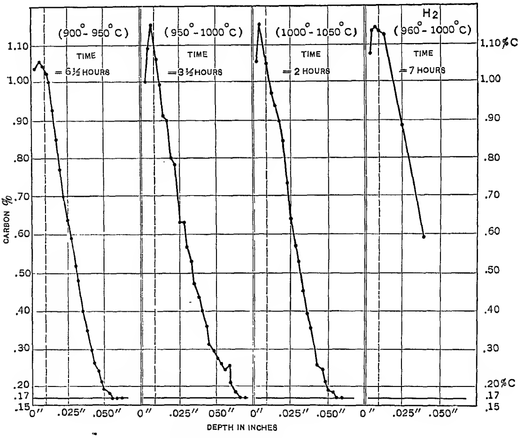

FIG. 119.—Diagram 4. "H."

tained at various temperatures with the Caron cement (carbon and barium carbonate).

The comparison of the first curve of the fourth diagram with the second and third curves shows clearly (especially if we take into account the length of the cementations) that this cement is more "sudden" the higher the temperature of cementation.

The fourth curve, corresponding to cementation carried out with cement already used previously for another cementation, confirms the fact that this cement does not become appreciably exhausted, or, rather, that it is regenerated spontaneously on remaining exposed to the air.

It is interesting to note here that the data just reported show that all four of the cements studied by Grayson, chosen by him from those considered best by "experts," furnish cemented zones containing marked hypereutectic layers and therefore subject to the phenomena of brittleness and exfoliation alluded to in the first part of this volume.

They also evidently confirm the fact, well known to all practitioners, that in cementations carried out with solid cements it is not practically possible to obtain with sufficient exactness a predetermined definite result by simply fixing the conditions of the cementation, such as temperature, time, etc. Hence the necessity of having means for controlling the course of the cementation *during* the operation. Such means is furnished by the so-called "*regulator test pieces*" of soft steel which are placed in the cementation boxes with the pieces to be cemented.

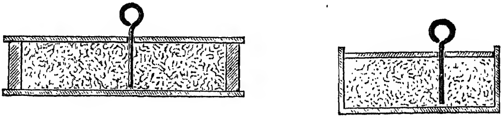

FIG. 120.

Usually, for the control of ordinary thin cementations (from 1 to 3 mm.), these test pieces are cylindrical bars 7–8 mm. in diameter, bent at one end into a hook. For the control of cementations of medium or great depth it is necessary to use bars of greater diameter.

The test pieces are introduced with their straight end in the cementation boxes, through holes having 1 to 2 mm. greater diameter. The arrangement of the test pieces in the cementation boxes is represented schematically in Fig. 120. Usually several test pieces are placed in every box and are removed, by means of a hooked rod, one at a time at definite intervals of time. Usually the examination of the test pieces is made by quenching them in water, breaking them near the end which was immersed in the cement and observing the surface of fracture. A more precise examination can be made by allowing the test piece to cool slowly, cutting it normally to the axis 1 to 2 cm. from the end which was immersed in the cement, polishing the section rapidly and etching it for some seconds with a 5% alcoholic solution of picric acid. On placing the section thus prepared in such a way that it reflects light toward the observer, and observing it with the naked eye or, better, with a simple lens, the "structure" of the zone is clearly seen, and from the presence and disposition of the needles of cementite, the masses of compact pearlite and the veins of ferrite, it is easy, for any one who has had some experience, to draw very precise conclusions as to the maximum concentration and as to the distribution of the carbon in the cemented zones, and hence as to the course of the cementation. This method also furnishes much more precise data than the examination of the surfaces of fracture of the hardened test piece as to the really *useful* depth of the cemented zone.

The examination of the polished and etched regulator test piece can furnish much more precise results when it is carried out with the microscope. This is possible, usually, only in plants of a certain size, having at their disposal a metallographic equipment. Moreover, the microscopical examination requires much more careful polishing of the surface to be examined.

Instead of the use of the various test pieces placed in a box and examined successively, Grenet[1] holds (and daily experience confirms fully the correctness of this opinion) that it is sufficient to place a single regulator test piece in each cementation box. In fact, when a known cement is used and the temperature of the furnace is tested from time to time (for example, by means of Seger cones), it is possible to predict with some approximation the time necessary to obtain the desired result; in ordinary cases and for the simplest and best-known cements, this approximation may be considered as being to about 30%. Suppose the regulator test piece to be removed and examined after about two-thirds of the time supposed necessary has passed; if the cementation has proceeded *normally*, the state of the test piece will be that which experience indicates corresponds to two-thirds of the operation. In this case the operation will be completed in the time predicted. If the cementation has proceeded with the *maximum rapidity*, the test pieces will be in the state corresponding to the final result required, and in this case the cementation is immediately interrupted. In all intermediate cases and in those in which the cementation has proceeded with exceptional slowness, the examination of the test pieces after two-thirds of the time supposed to be necessary will give sufficient data for an expert observer to be able to judge satisfactorily how much longer the cementation must still be carried on to obtain the desired result. In other words, the test pieces used in the way just referred to serve as indicators of the conditions under which the cementation is really proceeding.

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[1] Grenet, *Trempe, recuit, cémentation, et conditions d'emploi des aciers* (Paris, Béranger, 1911).

When the cementation boxes have large dimensions, Grenet advises the introduction of several test pieces at various points, and their removal all at once, so as to judge of the real course of the cementation in the various parts of the box.

Besides the regulator specimens just referred to, it is necessary, especially in cementations with solid cements, where the results are least certain, to place at various points of the box, near the objects to be cemented and similarly surrounded by the cement, "verifying specimens" (the so-called "*spies*"), usually consisting of cylinders of soft steel 10 to 15 mm. in diameter. Still more exact data are obtained by using "*spies*" made of the same steel as the pieces which are being cemented.

The examination of the fracture surfaces of these test pieces, removed from the boxes at the same time as the cemented pieces, and quenched together with them, while it constitutes a good guarantee of the satisfactory success of the operation, furnishes useful indications for modifying the conduct of succeeding operations so as to keep on improving the results.

As regards the cost of cementation carried out in boxes with solid cements, it is impossible to give figures of any general value, because the possible conditions of operation vary within too wide limits, either as to cost of the cement, consumption of fuel, consumption of boxes, etc. Moreover, often a small modification in the manner of carrying out a given operation (for example, the charging of the boxes in the furnace, the manner of allowing the boxes to cool, etc.) may change considerably the cost of the cementation.

If we wish to cite some approximately limiting figures, we may consider that the *complete* manufacturing cost (including, that is, interest and depreciation charges on the equipment, labor, general expenses, etc.) for the ordinary cementation of machine parts, carried out in boxes, varies in different works from a *minimum* of 20 centesimi (4 cents) to a *maximum* of 90 centesimi (18 cents) per kilogram of cemented pieces. (1.8 to 8.2 cents per pound.)

Finally, it is necessary to refer here briefly to another subject of practical importance; *viz.*, the protection of parts of the steel objects not intended to be cemented, or which should be cemented only slightly. The directions for this, for cementation carried out with solid cement, hold, in general, also for cementation with liquid, gaseous or mixed cements.

When solid cements are used, the intensity of the cementation can be greatly reduced or even stopped in the desired parts of the steel objects by covering the parts with a more or less thick layer of asbestos fiber. In the majority of cases, and especially when cements are used which, as the result of the high temperature, evolve carburizing gases, as, for example, Caron's cement, the protection afforded by asbestos is insufficient. In these cases more effective protection is obtained by refractory clay, mixed with a little water so as to form a dense paste which is spread in a more or less thick layer on the parts of the steel objects which it is desired to protect, and is then dried slowly before introducing these objects into the boxes. Even this means of protection has various disadvantages, among which the most serious is that of the insufficient adherence between the surface of the steel and the mass of dried earth, which very easily flakes off. Moreover, the porosity of the refractory earths is sometimes quite marked and is increased by the thin cracks produced as the result of the heat, so that the protection is often little better than that by asbestos.

To obviate these disadvantages, at least in part, it is sometimes customary to mix with the refractory clay a little graphite, which diminishes the "shrinking" on heating; this has the effect of diminishing the number and extent of the cracks formed in the refractory mass during the cementation.

Sometimes, on account of the special form of the pieces, it is necessary to keep the refractory earth in place by means of a metallic frame.

Grenet has recently recommended putty as the best means of protection.

A very sure means of attaining a practical result consists in leaving on the parts to be protected an excess of metal thicker by 0.3–0.5 mm. than the thickness of the cemented zone which is to be obtained and in then removing mechanically this excess of metal from the steel object after the cementation but before the quenching. It is clear that this method is very long and costly. It is practically applicable only in those cases in which the removal of the excess of carburized metal is exceptionally easy; for example, in the case of cylindrical objects, in which the removal can be effected on the lathe.

Another method, also expensive and applicable in practice only to objects of simple form, consists in "sheathing" the parts to be protected in a sort of case of soft sheet steel, adhering closely to the surface of the piece and of a thickness somewhat greater (from 0.4 to 0.8 mm.) than that of the cemented zone which is to be obtained. After the cementation and the quenching, the thin case, almost totally carburized, becomes brittle and can be easily removed by breaking it with a hammer.

The only case in which this method can be advantageously applied is that in which the piece to be protected has the form of a cylinder with at least one end free. In this case, in fact, protection can be obtained with relative ease by forcing the cylindrical piece into a tube of soft steel, heated to about 400° C. so as to suitably expand it.

Another process, apparently quite simple, is that patented by the works *de Dion-Bouton* of Paris. This consists in producing on the surfaces to be protected a deposit of metallic copper, obtained by simply washing these surfaces with an aqueous solution of copper sulphate, after first carefully washing with alcohol and ether so as to free them completely from the last traces of fatty substances.

However, under these conditions it is very difficult to obtain a continuous deposit of copper; the metallic skin, very thin and not adherent to the surface of the steel, is extremely delicate, so that a somewhat strong rubbing with the cementation powder is sufficient to tear it, which renders almost null the protective action of the copper. This delicacy is the consequence of the process itself of the "substitution" of the iron by the copper of the copper sulphate with which it is obtained. A more adherent deposit of copper can be obtained electrolytically by making the surface which it is desired to protect act as cathode in a bath of copper sulphate. The process is then more expensive and less simple, but gives good results, and may be applied with advantage to the partial protection of pieces of very complicated form.

In any case, however, the protection with copper can be adopted in usual practice only for cementations carried out at a temperature lower than 950° C. In fact, cementing at higher temperatures, the risk is run of reaching at any moment and at any point of the boxes the temperature of fusion of the copper, which is 1083° C. for pure copper kept out of contact with air but lower when the copper contains small quantities of foreign substances or of oxide.

The objects to be cemented are sometimes of such form that protection of the surfaces which must not be carburized can be obtained easily by simply placing them so that they touch each other along those surfaces. Such, for example, is possible in the case of a series of cylindrical gear wheels of the same diameter, which, when placed in a column surrounded by the cement, are cemented only in the toothed zone.[1]

§ 3. CEMENTATION WITH LIQUID CEMENTS

Leaving aside the use of fused cast iron as a carburizing material, which has been proposed several times but which at present is not applied, the only cements used in the liquid state consist of pure salts or of saline mixtures. Of these carburizing salts, the only ones commonly used are the simple or complex salts of hydrocyanic acid—the alkali or alkaline earth cyanides, the ferrocyanides and the ferricyanides.

Cementation with the cements just referred to can be effected by two clearly distinct processes, both furnishing only very thin cemented zones (in general not more than one or two tenths of a millimeter thick) of high carbon content. In other words, these cements are always very "sudden" or "quick."

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[1] We have already had occasion (see p. 57) to refer to attempts to find substances capable of impeding the carburization of definite regions of the surface of the pieces subjected to cementation.

Various references to the possibility of impeding locally the cementation by the use of definite substances ("anti-cements"), possessing specific "protective" properties, are found here and there in the literature. [See, for example, a note of Lecarme, in the *Revue de Métallurgie*, Vol. II, 1905 (*Mémoires*), pp. 516–525.] But thus far there have not been published precise data on the composition and properties of these substances, the precise knowledge of which would have, evidently, great practical importance.

The first process consists in immersing the objects to be cemented in a fused bath of the salt or of the carburizing saline mixture.

The second process consists in spreading over the surface of the object which it is desired to cement a mixture of the finely pulverized carburizing salt combined with other substances capable of giving to the mass sufficient fluidity and adhesiveness; then heating the piece thus prepared, for some minutes at bright red heat, generally in a simple forge fire.

The processes of both the first and the second group find useful application only when there is required in the cemented piece a high degree of hardness, and when it is not necessary to obtain those mechanical properties (resistance to shock, resistance to compression, etc.) which are incompatible with very thin carburized zones having a sudden decrease in carbon content, such as are obtained with liquid cements.[1]

The processes belonging to the first group may also be applied advantageously when it is essential to avoid as much as possible the deformations of the pieces during cementation and quenching, and to maintain their surface unchanged. Such is, for example, the case of engraved steel plates for printing.

It is easy to understand that the action of the liquid carburizing mass on the surface of the steel is considerably more uniform than that of a solid powdery mass, such as the solid cements, and than many of the gaseous cements now frequently used in practice. The latter, being gaseous hydrocarbons or the vapors of volatile hydrocarbons, decompose during the cementation, depositing thick layers of carbon in powdery or spongy masses on the surface of the objects.

As to the deformation of the pieces, it is known to be due especially to lack of uniformity of temperature either during cementation or more especially at the moment of quenching. But it is well known that the best way to uniformly heat a metallic piece is to heat it in a liquid bath kept at the desired temperature.

It is clear, therefore, that cementation *by immersion* in a fused carburizing bath is the process which is most suited to giving the best results.

The furnaces adapted to cementation by this process are, in general, quite simple, since there is no need of as exact and uniform heating of the laboratory of the furnace as with furnaces designed for operating with solid cements.

In fact, the fluidity and uniform temperature of the mass of the liquid cement are assured by the simple movements of heat convection, and overcome inequalities due to the more or less irregular way in which combustion may take place. It follows that in cementation with liquid cements the use of furnaces burning solid fuel is without such serious disadvantages as make its use difficult in other processes of cementation, such as the inequalities in the temperature of the laboratory and the danger of waves of high temperature.

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[1] We have seen (see p. 21) that Mannesmann had already made this observation.

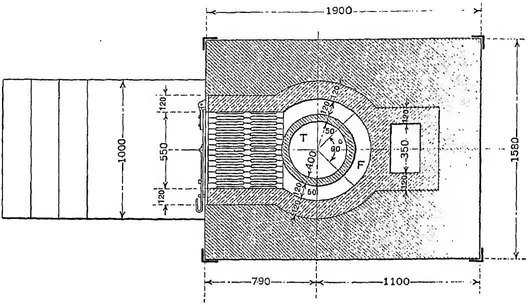

FIG. 121.

Notwithstanding this, however, the use of furnaces burning solid fuel is not widely diffused, even for using liquid cements, on account of the considerable time necessary to light them and set them in operation.

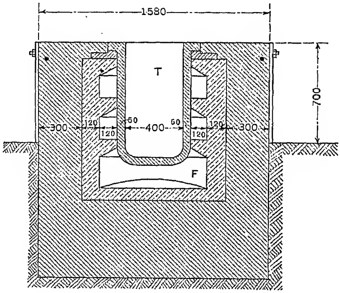

FIG. 122.

In almost all the furnaces designed for cementation with liquid cements *by immersion* the carburizing mass is kept fused in a crucible of cast iron or cast steel, of form and dimensions varying according to the shape and size of the pieces to be cemented, and heated from below or around the sides.

Most of these furnaces are similar to those usually employed for heating pieces to be tempered in a bath of lead or of salts. In cementation, however, it is necessary to provide good hoods and strong drafts for the more rapid removal of the vapors from the saline bath. When the bath contains considerable proportions of cyanides or ferrocyanides, the vapors consist of these salts, are strongly poisonous, and constitute a serious danger to the operator.

A furnace for cementation with liquid cements, heated directly with solid fuel, is shown in the figures 121, 122 and 123, taken from Reiser's volume, *Das Härten des Stahles.*

A furnace constructed according to these plans has given excellent results.

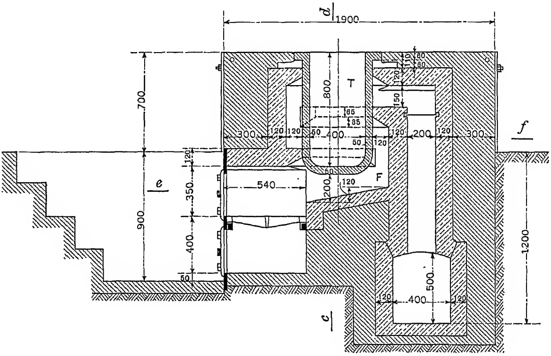

FIG. 123.

Fig. 124 represents a furnace heated with illuminating gas, constructed by the "American Gas Furnace Company," for cementation in a bath of fused potassium cyanide.

The burners *B*, arranged in two opposite series, direct the flames into the space between the refractory lining of the furnace and the steel crucible (shown separately, in *O*, near the furnace) in such a way that, whirling in this space, they envelop directly only the refractory material and not the crucible. The latter is heated, therefore, only by radiation, and is in part shielded from the strongly destructive action of the flames and from local superheating. The products of combustion issue from the laboratory through the flue *F*, which directs them into the large elbow-bend *H*, which leads them to the chimney. In this way there is produced in the flue *H* a strong draft toward the chimney, and since the flue *H* communicates at its lower end with the sheet-iron chamber *E*, which entirely covers the upper opening of the bath of fused potassium cyanide, all the poisonous vapors which are evolved are rapidly drawn toward the chimney as they are formed.

The following figure (Fig. 125) represents another illuminating gas furnace made by the same firm for the same purpose and on the same principles as the

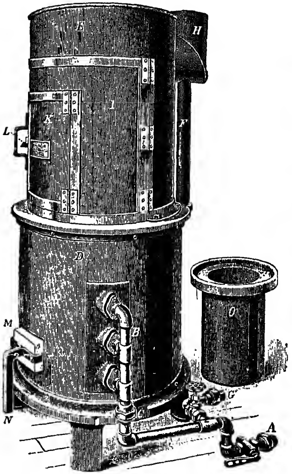

FIG. 124.

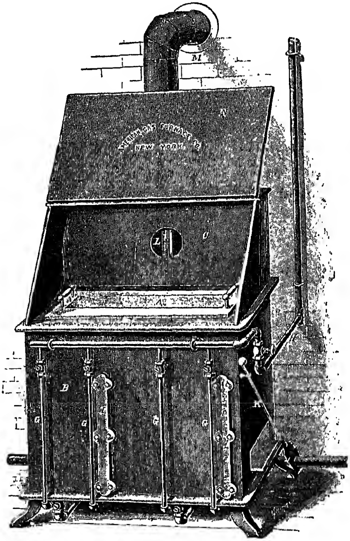

FIG. 125.

preceding one, but of a form adapted to the cementation of steel plates. To this end the crucible has the form of a rectangular prism, and since with a crucible of this form the circulation of the gases of combustion is more difficult and less regular, the four burners can each be regulated independently of the others, and each directs gas and air into the combustion chamber in the form of numerous small jets. In this furnace, also, the poisonous gases are drawn off in the same way as described for the preceding furnace.

The substance most frequently and almost exclusively used as liquid cement for cementation *by immersion* is potassium cyanide. In general, the pieces to be cemented are immersed in the already fused bath, kept between 850° and 900° C., and they are left in it from three to fifteen minutes, according to the depth of cementation desired.

If it is a question of pieces of medium size, say 1/2 to 3 kg. (1 to 6.5 lb.) and of not too irregular forms, the rule can be followed to immerse the pieces cold in the bath, and remove them when their temperature has exceeded 850°–880° C. In this way cemented zones of uniform thickness are obtained, from 0.03 to 0.10 mm. thick, according to the temperature and the length of the cementation. The concentration of the carbon reaches, near the surface of these pieces, 0.9 % or higher—sufficient to render them, after quenching, inattackable with the file. It is not advisable to try to obtain with this process cemented zones deeper than 0.15 to 0.20 mm., by prolonging the operation or carrying it out at a higher temperature, since there are then obtained cemented zones in which the excessive concentration of the carbon and its sudden variations give rise, after quenching, to intense brittleness and exfoliation. It is also necessary to remember the intensely poisonous properties of vapor of potassium cyanide—properties which render this process very dangerous.

Many other fusible carburizing mixtures have been proposed for use in place of the potassium cyanide in cementation *by immersion*, but, as far as I have personally been able to determine, I believe that none of these presents any advantages over potassium cyanide. The greater part of these mixtures have as base alkali ferrocyanides and ferricyanides, frequently mixed with potassium bichromate.

Besides the cements acting in the state of complete fusion, like potassium cyanide, some *partially* fusible cements have been proposed, to be used in an analogous manner. In the many mixtures of this kind repeatedly proposed, the infusible constituent is generally carbon in its various forms, such as *coal*, *coke*, etc., while the fusible portion is formed of salts such as alkali cyanides, ferrocyanides, carbonates, etc. As an example the mixtures indicated in the German patent No. 237492 (Kl. 18c. Gr. 3, 1911), consist of sodium carbonate (about 15%), while coke and calcium carbonate constitute the infusible portion.

The variety of mixtures proposed for cementation by the second process is considerably greater; using these "*carburizing varnishes*," the conditions which the mixture must satisfy are considerably more difficult of realization than those for a fused bath. In fact, besides possessing efficacious carburizing properties, the "*varnish*" cement must adhere well to the surface of the steel, even during the heating; it must not burn easily; and after the ignition it must be removable without too much difficulty from the metallic surface, leaving it as smooth as possible.

The simplest of the cements to be used by sprinkling over the surface of the pieces to be cemented is finely powdered potassium ferrocyanide. It is sprinkled on the piece to be cemented heated to redness; the piece thus prepared is again placed in the forge fire and the heating is continued until all the ferrocyanide is melted; then the piece is quenched in water. There are used in the same way various mixtures of potassium ferrocyanide with potassium cyanide, potassium bichromate, or ammonium bichromate.

Even without pulverizing the carburizing mixtures to a very fine powder, good results can be obtained by working as follows The piece to be cemented, first well polished, is heated to about 800° C. and immersed in the powdered carburizing mixture, turning it several times until it is well covered with it; then it is again heated to 800° C. and again immersed in the powder. The operation is repeated until the cement forms on the piece a compact layer of sufficient thickness. In general, two heatings suffice. Then the piece is heated until the cement melts, and is quenched at about 800–850° C.

In all cases it is necessary to take care that during the heating which precedes the first immersion in the carburizing powder there is no oxide formed on the surface of the steel which would hinder the succeeding cementation. This can be assured by not heating too intensely and, when working in a forge fire, by carefully protecting the steel by pieces of coal or even by means of an iron tube from the direct action of the air blast, which, in any case, must be kept as gentle as possible.

Among the mixtures proposed for use as "*varnishes*," containing infusible constituents, together with the fusible ones, we may cite the following:

(*a*)	Powdered potassium ferrocyanide	2 parts
	Powdered potassium bichromate	1 part
	Dextrin paste (as much as is necessary to obtain a pasty mass).	

This cement, very rich in potassium ferrocyanide, is dangerous on account of the violent poisonous action which it exercises if it comes in contact with even slight scratches in the skin. It is therefore necessary for the worker using it to protect his hands with rubber gloves.

(*b*)	Potassium cyanide	5 parts
	Sodium borate	2 parts
	Potassium nitrate	2 parts
	Lead acetate	1 part
(*c*)	Animal charcoal	20 parts
	Horn filings	6 parts
	Potassium nitrate	8 parts
	Sodium chloride	40 parts
	Glue	5 parts

These two mixtures are used in the state of powders in one of the ways indicated above.

(*d*)	Calcined horn scrapings	16 parts
	Cinchona bark	8 parts
	Yellow prussiate of potash	4 parts
	Potassium nitrate	2 parts
	Salt	4 parts
	Black soap	30 parts

The ingredients are mixed in a mortar, forming a paste, which is then dried. To use it, it is diluted with water until it forms a dense liquid which is spread by means of a brush on the objects which it is desired to cement.

It is easy to find a large number of recipes similar to these in manuals on case-hardening and cementation. The more complicated ones are, in general, not worth more than the simpler ones which I have cited above. The cemented zones which are obtained with cements used as "*carburizing varnishes*" do not exceed, in general, a thickness of 0.05 to 0.15 mm., and show individual characteristics entirely similar to those of the zones obtained with liquid cements used "*for immersion*;" their uniformity in the various regions of the cemented surface is, however, considerably less.

§ 4. CEMENTATION WITH GASEOUS CEMENTS

Only within the last four or five years have the processes of partial cementation of steel based on the use of gaseous carburizing substances been generally applied. Before then they may be considered as having been limited, save for a few rare exceptions, to very deep cementations, more than 20 mm. thick, such as those on armor plates.

If we leave aside these special cases, it may be said that the technical applications of cementation with gaseous cements have developed simultaneously with the studies which cleared up their true mode of acting; that is, within the last four or five years.

The first part of this volume has already dealt with the properties of the various gaseous cements, their various modes of acting, the characteristics of the various types of cemented zones which can be obtained with them, and with the great variety and the certainty of the results which a proper use of these cements assures. The information thus set forth contained all the data for properly performing cementation with gaseous cements, both as regards the choice of the cement in relation to the composition of the steel to be cemented, the type of cemented zone which it is desired to obtain, and the most suitable conditions of temperature, pressure, velocity of the gaseous current, etc., which it is necessary to use to cement a given steel with a given gaseous cement to obtain a certain desired result.

In the present chapter we will limit ourselves, therefore, to making brief reference to the apparatus used in practice for cementation with gaseous cements, together with a summary of the methods used to produce "typical" gaseous cements whose carburizing action is well defined and exactly controllable.

Of the few types of furnaces for cementation with gaseous cements at present used in plants of considerable importance, I shall refer only to two, with which I have been able to experiment personally for a long time.

The first is made according to the designs of Machlet by the "American Gas Furnace Co." of Elizabeth, New Jersey, United States of America.

The complete equipment comprises two separate parts: the cementation apparatus proper and the apparatus for the production of the carburizing gas. We shall see shortly, however, that the cementation apparatus may also be used with other carburizing gases than that proposed by the inventor. At any rate, I shall briefly describe both apparatus.

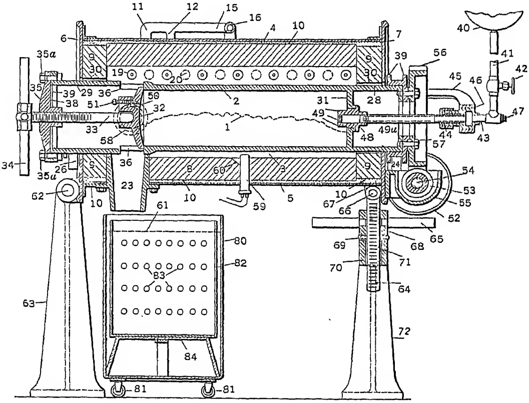

FIG. 126.

The Machlet cementation apparatus, a longitudinal section of which is shown in Fig. 126, consists essentially of a furnace laboratory in the form of a cylinder placed horizontally. In the interior of this, and placed coaxially with it, is the cylindrical steel crucible 2, whose ends protrude from the furnace (leaving a small space between the steel walls and the circular openings made in the two ends of the laboratory) and rest on two pairs of rotating rollers. The crucible, which constitutes the cementation chamber, is kept slowly revolving during the operation by means of the toothed wheel 56, fixed at one of the ends and engaging with the endless screw 53, controlled by a chain drive.

In the upper part of the laboratory of the furnace there are gas burners 19–20, arranged alternately in two series along two generatrices of the cylindrical body of the furnace, as indicated in Fig. 127, in transverse section.[1]

The illuminating gas is burned by air under pressure and the flames, circulating in the space between the refractory lining of the furnace and the walls of the retort, heat the latter uniformly to the desired temperature.

In the retort are two steel disks, 31 and 32, arranged in such a way as to retain the objects to be cemented, placed between them, in that part of the retort which is heated uniformly to the temperature suitable for the cementation. The two disks are traversed at their center by two tubes, one for the entrance of carburizing gas into the retort and the other for the exit of gas.

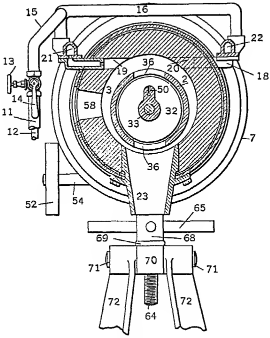

FIG. 127.

The metallic parts of the apparatus which might be heated to a high temperature are protected by linings of asbestos and of fire-clay; some of these linings are seen in Fig. 126.

The charging of the furnace is done easily by removing the door 35 (kept in place by simple set screws), and together with it the disk 32. The pieces to be cemented are then put into the cementation chamber, and the furnace closed for the cementation. Then, slowly revolving the retort 2, heated to the suitable temperature, the carburizing gas is circulated through the apparatus.

This apparatus is adapted especially well to superficial cementation of very small objects which are to be cemented all over, such as chain links, small buckles, small axles, bolts, threaded cutting dies, etc.

In fact, it is quite difficult to cement well objects of this kind with other apparatus, in which it is necessary to surround them carefully with solid cement, or to place them on special supports in such a way that their surface may be totally enveloped by the carburizing gases, when gaseous cements are used. In both cases the operations are much longer, and therefore more costly, than they are with the Machlet furnace, where the objects may be rapidly piled in, without special placing.

The Machlet furnace is less advantageous for the cementation of large pieces, especially when they must be protected from carburization at parts of their surface, or when two of their dimensions are exaggerated with respect to the third.

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[1] This apparatus is protected by patents in the majority of countries. The drawings are from the German patent 191394 of 1907 (class 18c.).

In fact, protection of the parts which must not be cemented cannot be efficaciously obtained in the Machlet apparatus, either by using layers of refractory earth or by means of layers of electrolytic copper, for none of these protective substances resists the repeated shocks which each of the pieces charged into the retort receives from the other pieces by the rotation of the retort, and their continually rolling over each other. It is necessary, therefore, to use in this case one of the two quite costly and difficult processes which I have already described (see p. 278), either protecting by "cases" of steel or by a layer of excess metal to be mechanically removed after the cementation and before quenching.

In various cases, it is true, it is possible to collect the different pieces into "bundles," held together by means of straps and screws, so that they shall touch each other along the surfaces which must be protected from the action of the carburizing gases. But the necessity of making "bundles" of considerable dimensions, so as to reduce to a minimum the number of the pieces forming the ends of each bundle (which, as is evident, have no protection) makes the rotation of the cementation chamber useless, and causes other disadvantages.

If we except the cases in which the pieces to be cemented are of approximately spherical or very elongated cylindrical form, in which cases the pieces "roll" easily over each other during the rotation of the retort, the very large pieces undergo, by the rotation of the retort, successive "falls," which result in harmful shocks against each other and against the walls of the retort. The damage produced by these shocks is evidently more serious the more irregular the form of the pieces and the more delicate their outline.

If the pieces have a "flat" form, they end by arranging themselves in the retort in such a way that one of their faces lies on the wall of the retort and slides along it, always adhering to the wall of the retort and never subjected to the desired degree of carburizing action of the circulating gases. Such is the case with disks for king-pin bearings, cups for ball bearings, sectors, keys for dies, etc.

In these cases it is sometimes possible to make up the objects to be cemented into bundles of large dimensions having approximately the form of very elongated cylinders; these are placed with their axes parallel to that of the retort and roll regularly during its movement. The objects in question can also be fastened to other suitable objects which modify, so to speak their form, making the rolling in the rotating retort easier.

Whichever of these expedients is adopted, however, we always have the disadvantage of markedly increasing the weight of the object to be cemented. When it is desired to use supports or bundles, the rotating cementation chamber becomes practically useless.

The Machlet furnace, used for the cementation of small pieces under the conditions referred to, gives excellent results and permits of cementing in very large numbers pieces which, by reason of their small size and low price, could not be conveniently cemented by other methods. In these cases the complete treatment has been made still more easy and economical by the use of ingenious apparatus for automatic tempering, devised and made by the same firm which manufactures the Machlet furnace.

In the large Machlet furnace the available space in the cylindrical retort is 120 cm. long by 38 cm. diameter. In the smaller furnace made by the "American Gas Furnace Co." this available space is 75 cm. long by about 18 cm. diameter.

The manufacturers guarantee that the furnace of small model may be used for the cementation of pieces up to 15 cm. in diameter and 50 cm. in length, with a consumption of about 10 cubic meters (350 cu. ft.) of illuminating gas per hour. The firm does not say what depth the cementation is designed to reach in one operation, but it is to be supposed (and experience confirms this) that this depth is about the average ordinarily required for machine pieces; that is, from 0.7 to 1.2 mm. The retort of this small furnace costs little more than 100 lire ($20). It is said to last for about 400 hours of heating under the above conditions. The larger furnace consumes about 15 cubic meters (525 cu. ft.) of illuminating gas per hour. Its retort costs about 250 lire ($50) and also lasts, on an average, about 400 hours.

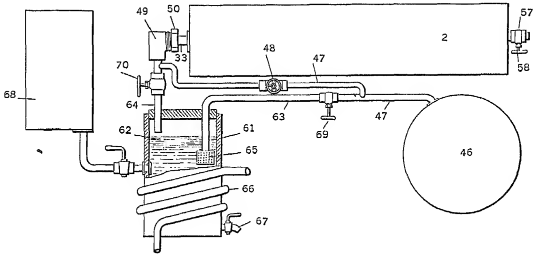

FIG. 128.

The apparatus which the "American Gas Furnace Company" constructs for the production of the carburizing gas necessary for the operation of the Machlet furnace is also patented. It is based on the idea of "diluting" the carburizing vapors of oils of various densities, petroleum, etc., with an "inert gas" which acts as a "vehicle" for the carburizing gases, carrying them into the cementation chamber, and preventing their forming a deposit of carbon by their decomposition at the high temperature of the cementation. This deposit might be so abundant as to obstruct the tubes and the interstices through which the carburizing gases must circulate.

A diagrammatic section of the apparatus is reproduced in Fig. 128, taken from the German patent No. 236007 (Kl. 18 cs. Gr. 3, 1911).

The receptacle 61 contains the carburizing liquid whose vapors are to be carried into the cementation chamber, the rotatory retort 2, through the action of the inert gas coming from the receptacle or generator 46. The inert gas bubbles through the liquid 62, reaching the latter through a distributor 65, which admits it into the liquid in the form of small bubbles. The carburizing liquid can be heated by means of the spiral 66 so as to increase at will the proportion of its vapors which, all other conditions being equal, are carried by the inert gas into the cementation chamber. To regulate with greater precision and within wider limits the proportion of the carburizing vapors carried by the inert gas into the cementation chamber, use is made of the connecting tube 47 and the stopcocks 48 and 49, arranged as indicated in the figure. By suitably regulating these, it is possible to modify at will the relation between the volume of inert gas which reaches the cementation chamber after having bubbled through the carburizing liquid and that which reaches it directly without carrying carburizing vapors; in this way it is clear that it is easy to regulate with great precision the amount of the carburizing vapors which reach the cementation chamber with a given volume of the inert gases.

The quantity of carburizing liquid contained in the receptacle 61 is kept constant by the reservoir 68, connected to it by an easily regulated stopcock.

The same patent just referred to also claims, inversely, making the carburizing gas bubble through a liquid in the receptacle 61 capable of developing inert gases, adapted to diluting the carburizing gas which reaches the cementation chamber 2. As a liquid capable of developing an inert gas, the patent names ammonia water. I do not know whether this second procedure has found practical application.

In the apparatus made by the "American Gas Furnace Co." the *inert* gas is producer gas.

In general, one gas generating apparatus is sufficient to furnish the cement for two cementation apparatus.

As to Machlet's choice of the composition of the carburizing gas we have seen on p. 184 that the most efficacious "vehicle" for the diffusion of carbon into the solid steel is carbon monoxide, and that nitrogen, hydrogen and other inert gases produce this diffusion only to a very small and practically negligible extent. We have also seen and given the very simple theoretical reasons why hydrocarbons are very "sudden" cements and shown that this characteristic is profoundly modified when they act in the presence of carbon monoxide. This modification may, with increase in the proportion of the carbon monoxide, become so marked as to produce "mild" cements, whose "intensity"

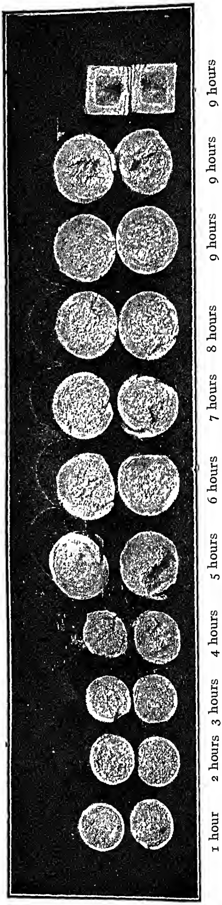

Fig. 129.

can be regulated when the concentration of the carbon monoxide is such that it plays the major part in the carburizing action of the gaseous mixture. The hydrocarbon then intervenes only as a modifier of the conditions of equilibrium of the system carbon monoxide-carbon dioxide-carbon in solid solution in the γ-iron. On these conditions of equilibrium depend the concentration and the distribution of the carbon in the cemented zone. From these known facts it can be deduced *a priori* that the action of the cement proposed by Machlet, in which the *inert* gas does not contain such a strongly preponderating quantity of carbon monoxide as is necessary to radically modify the specific carburizing action of the hydrocarbons, must be entirely similar to that of the hydrocarbons used alone. The use of this cement, therefore, can show no other advantage, as compared with the simple hydrocarbons, than that of producing a smaller deposit of pulverulent carbon from the decomposition of the carburizing gas. This last advantage, which certainly has great practical importance, is obtained equally well with the gaseous cements with carbon monoxide as base; these, however, present the far greater advantages of furnishing "gradual" cementations which can be regulated with precision and certainty, even as regards the concentration and distribution of the carbon, and of preserving the efficacy of "penetration" of the carbon even when the cemented zone has reached a considerable depth. This latter characteristic, which manifests itself to an even more marked degree in the "mixed cements" with carbon monoxide as base, is due to the specific action of the carbon monoxide acting as a "vehicle" for the diffusion of the carbon into the iron.

What I have just said is fully confirmed by the examination of the fracture surface of the specimens cemented with those cements and quenched. Fig. 129, taken from a booklet illustrating the Machlet process and published by the "American Gas Furnace Co.," represents the surfaces of fracture of a series of specimens cemented in the Machlet apparatus during the periods of time indicated under each specimen, and hardened. In all the specimens there is to be seen a sudden variation in the structure of the steel at the line of passage from the cemented zone to the material of the "heart" of the piece, which has remained soft; a variation corresponding to the rapid decrease in the carbon content due to the special mode of action of the hydrocarbons used as cements. We shall see later that this harmful phenomenon does not show itself in the cemented zones obtained with mixed cements having carbon monoxide as base.

It is also to be seen clearly in the same figure that the depth of the cemented zones increases only to a very slight extent beyond a certain limit which, under the conditions under which the specimens here reproduced were cemented, is reached after five hours of cementation.

To conclude, the Machlet apparatus of the "American Gas Furnace Co." is excellent from all points of view and can be used with the greatest advantage whenever thin cemented zones are to be obtained in large numbers of objects of small dimensions of such a kind that they are not to undergo violent shocks after hardening. The high carbon content of the cemented zones obtained imparts to the cemented and hardened objects a maximum resistance to wear by friction.

The Machlet furnace, independent of the special carburizing gas generator described, can be used very advantageously to cement with the gaseous cements having carbon monoxide as base, on condition that the pieces to be cemented are of suitable form and dimensions. In this case there can be obtained with this furnace cemented zones with perfectly "gradual" variation in the concentration of the carbon, and therefore such as present, after hardening, maximum resistance to shock.

The second type of furnace for cementation with gaseous cements is entirely similar to that especially designed for cementation with "mixed" cement having carbon monoxide as base. Briefly, it has fixed, vertical, cylindrical muffles, heated with producer gas from a coke gas producer built in the body of the furnace itself. An efficient system of regenerators permits of heating a sufficiently large section of the muffles placed in this laboratory to a uniform and constant temperature, which can be exactly regulated, ranging between 800° and 1200° C.

Fig. 130 represents a vertical section of a two-muffle furnace of this type. The figure also shows the apparatus for charging and discharging the pieces to

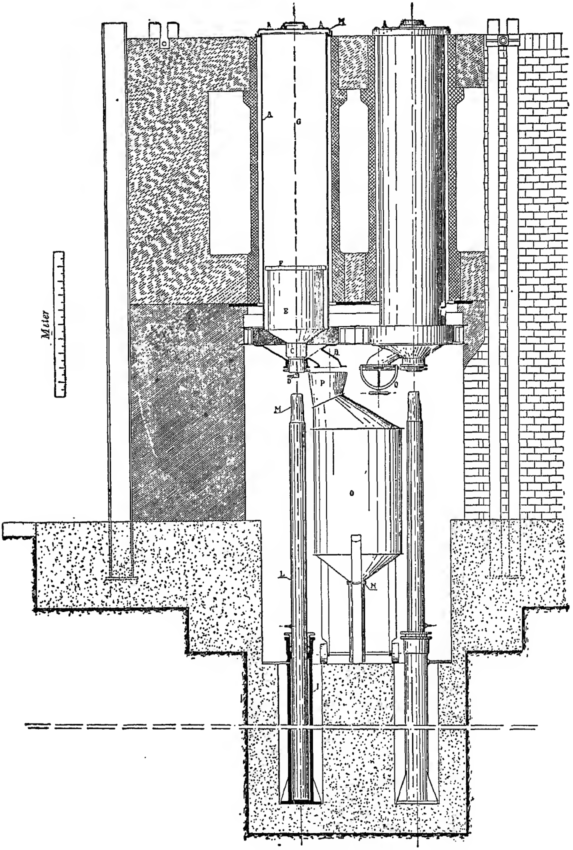

FIG. 130.

be cemented—the same as are used for cementation with "mixed" cement. Fig. 131 shows the outside of one of these same furnaces constructed by

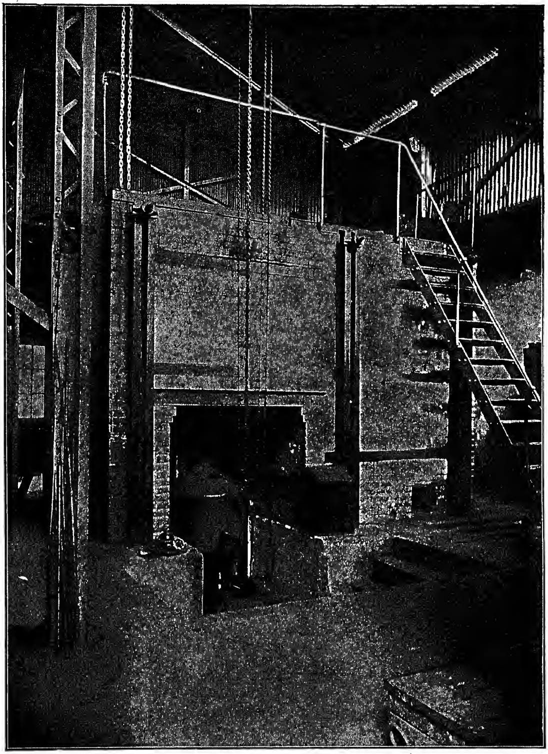

FIG. 131.

"Ch. M. Stein" of Paris in the Sampierdarena Machine Shops of the "Società Anonima Italiana Giov. Ansaldo e Co.," owner of patents on the apparatus and the processes of cementation for which they are especially constructed.

The construction of the furnace proper, or of those parts of it which act as heating apparatus, presents nothing essentially new, but consists of the ordinary parts for production of gas, combustion, regeneration of heat, regulation of temperature, etc., etc., and is designed with particular care so as to obtain maximum uniformity in temperature in the operating parts of the muffles. In a furnace of the dimensions shown these operating parts are the central portion of these muffles, about 1.20 mteers long. Moreover, efficient devices for the regeneration of heat make it easy to keep constant the temperature of the laboratory and of the muffles in it for a practically indefinite time, at any point within a wide interval of temperature. In the interior of the muffles the temperature can be kept constant between 800° and 1200° C. with a tolerance of 10°, and with differences between the various points of the useful zone not greater than 10° C.

It is proper to furnish some more details as to the structure of the accessory apparatus represented in Fig. 130, for while they lend themselves very well to cementations with gaseous cements, they have been studied especially for cementation with the mixed cements having carbon monoxide as base. The dimensions of the individual parts shown in the figure can easily be obtained from the metric scale given in the drawing. We call attention to the fact, however, that furnaces of this type are constructed of various dimensions, according to the special purposes for which they are intended.

In the interior of each of the muffles of refractory material is placed a cylindrical retort of soft steel *A*, whose external diameter is about 10 to 20 mm. smaller than the internal diameter of the muffle.

Seamless Mannesmann tubes, which can easily be found on the market up to a diameter of about 35 cm., serve well as retorts. For greater diameters, such as are shown in the furnace in the accompanying figure, autogenously soldered sheet-iron tubes are used.

The retort is supported by a base ring connected with a frame fixed in the wall of the furnace. The setting of the retort to the base ring and to the upper ring *H*, designed to receive the cover, is such as to permit of substituting one retort for another in a few minutes. To the base ring is also fixed a funnel of special shape *B*, of cast iron, closed at the bottom by a slide-valve *Q*.

The special form of this funnel, and especially the side neck and the slide-valve, are provided for the use of mixed cement. Through the wall of the funnel passes, through a tightly fitting stuffing box, the steel tube *C*, for the admission of the carburizing gas. This enters through the side tube *D* which is screwed, during the cementation, to the middle of the piece *C*. This is connected with the hollow cylinder *E*, of cast-steel, designed to support the pieces to be cemented on the disk of steel and refractory material *F*. The carbon monoxide, after having passed through a hole made along the axis of the piece *C*, reaches a small distributor placed inside *E*, and then passes into the cementation chamber *G* through numerous holes made in the disk *F*. During the cementation, the cylinder *E* rests on a series of projections on the same base ring to which is fixed the funnel *B*, so that, during the cementation, this ring must support the whole weight of *E*, of the disk *F*, and of all the objects to be cemented which rest directly or indirectly on this disk *F*. The section in Fig. 130 shows the position of the various parts during the cementation.

The method of charging the retort varies markedly according to the dimensions and forms of the objects to be cemented, so that it is not possible to give general rules. We will therefore limit the directions to those which hold for some special examples.

Supposing that cylindrical gear wheels whose maximum diameter is only 100–150 mm. less than the internal diameter of the retort are to be cemented.

The tube *D* is first unscrewed; then, by means of the plunger *L*, controlled by the hydraulic cylinder *I*, the whole of the parts *C*, *E*, and *F*, into which the plunger fits in rising, with its truncated conical end *M*,[1] is raised. When the piston has reached its limit, and the upper surface of the disk *F* is only about 30 cm. below the cover of the retort, the cover *H* is removed and the wheels to be cemented are placed "in column" on the disk *F*, arranging them horizontally, one above the other. As the wheels are put in place, the plunger *L* and with it the pieces *C-E-F* are lowered and the charging is complete when the apparatus has reached its lowest position, indicated in the figure. In this position, the last wheel charged must be at least 30 cm. from the upper edge of the retort. In general, the objects to be cemented are charged already heated to about 800°–900° C., which realizes very great advantages, both as regards the quality of the product and economy and regularity of the operation. For the preliminary heating of the pieces to be cemented, use may be made of a small muffle furnace heated directly with coal, since the uniformity of temperature which can be obtained with such a furnace is more than sufficient for this special purpose. Sometimes, especially when it is not necessary to push the cementation furnace to its maximum production, one of the vertical muffles may be used for the preliminary heating of the objects to be cemented while in the other the cementation of the preceding charge is effected. In this case, a better utilization of the furnace is obtained by using each of the muffles alternately for the cementation and for the preliminary heating of the pieces.

Good results are also obtained, when the pieces to be cemented are not of too large dimensions, by using for the preliminary heating a series of apertures made in the refractory wall between the gas producer and the laboratory of the furnace.

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[1] The plunger *L M* is cooled internally with a current of water so as to prevent its becoming too hot in case it should accidentally remain in the retort for too long a time.

When the pieces to be cemented are put in place, in the manner indicated, the retort is covered, carefully luting the edges of the cover so as to obtain perfect closing. Then the plunger *L* is lowered entirely, the tube *D* is screwed to the piece *C*, and the carburizing gas is slowly admitted to the distributor *E* and from this to the retort. The gases of the retort, displaced by the fresh carburizing gas which enters through the distributor *E*, issue through the little tube fixed on the cover *H* of the retort.

In case it is desired to use cements with carbon monoxide as base, which present great advantages, a thin metallic tube is fixed co-axially in the tube *D*, with its longest arm penetrating into the distributing apparatus. This tube passes out from the lowest part of the elbow joint of the tube *D* and penetrates into the interior of the apparatus as far as the distributor of the carburizing gas. The volatile hydrocarbon (benzene, ligroin, etc.) is sent into this tube in the desired quantity, exactly regulated by means of a very sensitive regulator stopcock. Its carburizing action is to modify to the desired extent, according to the rules which I have already pointed out, the specific action of the carbon monoxide which is admitted through the tube *D* into the cementation chamber. Since the little tube carrying the hydrocarbon penetrates through the tube *D* into a region of the retort heated to a temperature (300°–400°) much higher than the boiling point of the hydrocarbon, the latter is already totally in the state of vapor when it mixes with the carbon monoxide.

The velocity of the current of carburizing gas, whether carbon monoxide or another gas, which passes into the tube *D* is indicated constantly by a small apparatus like an anemometer, inserted in the tube carrying the gas. The quantity of gas used is controlled by a meter; for this purpose ordinary illuminating gas meters, of the type called "dry," serve very well.

When the operation has been carried on for a sufficiently long time, with continuous control of the temperature and the composition and quantity of cementing gas which circulates through the retort, the gaseous current is interrupted. The small cover which closes the central opening of the large cover of the muffle is then opened, and the gas issuing from it is quickly lighted; then the large cover is removed and the gas contained in the muffle is allowed to burn. In this way the slight explosion is avoided which the usual carburizing gases would produce if they were lighted after they had mixed with a considerable proportion of air. This being done, all that is necessary is to unscrew the tube *D*, raise the plunger *L* until the terminal cone *M* fits into the hollow of the piece *C*; then the hydraulic cylinder *I* is kept slowly working so as to gradually raise the platform *C*, *E*, *F* with the cemented pieces on it. Then a workman, standing above the furnace near to the upper opening of the muffle, takes the cemented pieces as they come near the opening of the muffle and quenches them in the basin which is also placed above the furnace; if it is desired to harden afterward, she may bury them in hot ashes. All the cemented pieces having been removed in this way, the furnace is ready for a new charge.

The arrangement of the pieces to be cemented in the retort varies with their form and with their dimensions. Pieces of cylindrical form can always be placed "in column" in a manner similar to that described in the example just cited. If the diameter of the objects is small (toothed pinions, drills, rings for ball bearings, etc.), several "columns" can be made in a single charge, but in this case it is well that the pieces be kept in position by rods of iron, upon which the pieces are strung, if they are to be cemented externally (drills, pinions, etc.). For cylindrical pieces to be completely cemented, such as rings for ball bearings, the rods are arranged on the outside of the "column." Pieces of very elongated and irregular form are placed in the retort with suitable supports. Finally, very small pieces are placed in "baskets" formed of iron strips or rods joined together by a network of iron wire. It is well to point out at once that the furnace with fixed cementation chambers, with which we are now dealing, is not well suited for the cementation of very small and very numerous pieces, when used with a gaseous cement. This limitation of the furnace with fixed chambers disappears when it is used for cementing with mixed cement having carbon monoxide as base.

Besides the case just referred to, the furnace with vertical muffles is well suited to the cementation of pieces of considerable dimensions, whether they are single pieces or "bundles" of smaller pieces. This is true even when the pieces or the bundles have very irregular forms or present delicate projections. For pieces of this kind, which are easy to place so as to leave between them large spaces, permitting easy circulation of the carburizing gases, experience shows clearly the uselessness of imparting to the retort any movement whatever, for it would in no wise increase the uniformity of the cemented zone.

A furnace of the type described and of the dimensions represented in the accompanying figures, in which the useful space in each of the two muffles has a diameter of about 45 cm. and a length of about 1.20 m., consumes about 450–500 kg. of ordinary gas-works coke per twenty-four hours when the relatively high temperature of 1100° C. is maintained in the interior of the muffles. For the lower temperatures usually employed, the consumption of fuel is markedly less.

By using gaseous cement with carbon monoxide as base and by working at a temperature near 1000° C., the cemented zones of the thickness usually required for machine pieces (about 1 mm.) are obtained in less than two hours. Counting the time necessary for charging and discharging the pieces, ten cementations per muffle can be made in twenty-four hours. It is seen that the cost of fuel is quite low.

As to the cost of the carburizing gas, that naturally depends on the quality used. In many cases, for example, when gaseous cements with carbon monoxide as base are used, the cost of the cement can be greatly reduced by collecting the gas which issues from the cementation chambers[1] in suitable gasometers and using it again. Before using again, however, it must be subjected to a simple and inexpensive process of purification, varying according to the composition of the gas and the manner in which it has been used. The expense due to wear of the fixed retorts is also quite small, especially when compared with the corresponding expense for the rotating retorts.

Steel retorts, of the kind described, cost from 32 to 40 centesimi (6.4 to 8 cents) per kilogram (3 to 3.5 cents per pound) and weigh, in a furnace of medium dimensions such as described, about 300 kg. (660 lb.). By making a good refractory lining in the space between the steel retort and the refractory muffle, a retort may last from five to eight months when the furnace is continuously heated to 1000° C.

The principal advantages of gaseous cements lie in the ease and certainty with which it is possible to uniformly cement all over pieces of steel of very complicated form and having re-entrant angles and very narrow and deep cavities, such as slits or holes. Similar results can also be obtained with the use of mixed cements with carbon monoxide as base.

Besides these advantages, the use of gaseous cements presents the other great practical advantage, common also to the mixed cements, of not involving, as do solid cements, the use of cementation boxes charged with cold materials. This obviates the disadvantages of the high cost, slow heating, great deformations of the cemented pieces, etc., which are inevitable in cementation in the ordinary boxes.

In cementation with gaseous cements, and especially when use is made of carburizing gases of simple and accurately known composition, such as those with carbon monoxide as base, it is relatively easier to predict the results which will be obtained by working under definite conditions. When the temperature in the cementation chamber is accurately controlled during the whole operation, for example, it is not necessary in the majority of practical cases to make use of control specimens, which are indispensable in cementation carried out with the ordinary solid cements. This necessity of control by means of test pieces immersed in the solid cements is partly due to the irregularity in the action of these cements caused by variations in the compression of the cement on the surface of the steel, differences in the degree of pulverization of the cement, etc. It is also due to the impossibility of knowing, from the temperature of the laboratory of the furnace or of the muffles containing the boxes, the temperature reached at successive intervals of time in the various parts of the charge, since the velocity of propagation of the heat in the mass of the cement varies within very wide limits with variations in the state of division, of compression, etc., of the cement.

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[1] In the furnace with vertical muffles which I have described above, the gas which issues from the retorts can easily be recovered by attaching a flexible tube to the exit tube of the gas, fixed, as indicated in the figure, to the cover *H* of the muffles.

The data given in the first part of this volume establish the results which can be obtained under the conditions usually realized in practice, with several of the more important types of gaseous cements; it is useless, therefore, to further discuss this point.

For every new "type" of gaseous cement which it is desired to use, a few preliminary experiments suffice to establish with precision under what conditions of temperature, pressure, velocity of the gaseous current, etc., the cementation must be carried out to obtain a definite result. This result, contrary to the case of the solid cements, can then be always reproduced sufficiently close for the demands of practice.

Many inexact data are found in print as to the carburizing action exercised by various gases on steel. The use of these data might easily give rise to failures in practice. An example is given in the first part of this volume (p. 67)—the results obtained by Bruch on the carburizing action of carbon monoxide. Another is the data contained in a table given by Lake, on p. 233 of his volume: *Composition and Heat Treatment of Steel*.[1] This table is taken by Lake from a publication by J. C. Olsen and J. S. Weissenback of the Polytechnic Institute of Brooklyn, and contains assertions such as the following: pure acetylene gives cemented zones of very slight hardness but, when used mixed with ammonia, it gives very hard cemented zones; methane, both alone and when combined with ammonia, gives very faint cementations; carbon monoxide, even when used alone, gives the cemented zones which are hardest and have the highest carbon content, etc. Now, these statements, as well as many other conclusions which would seem to result from the data contained in the table, are completely erroneous, being contrary to the results of daily practice, and being negatived by the repeated and accurately controlled work by various experimenters reported in the first part of this volume.

As regards the characteristic mode of action of the gaseous cements, we may, in general, consider Mannesmann's observation (see p. 21) as correct, limiting it, however, exclusively to the case of the hydrocarbons. According to this, the gaseous cements are suited only to obtaining superficial cementation. We have seen, however, that the reason for this fact must certainly not be sought in the assumption of Mannesmann that the gases find difficulty in "circulating in the pores" of the metal.

This same observation is, on the other hand, completely inapplicable to the gaseous cements whose major carburizing action is due to carbon monoxide. In fact, these cements can furnish very deep and perfectly

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[1] McGraw-Hill Book Co., New York, 1911.

"gradual" cementations even when using them at very high temperatures so as to obtain very rapid penetration; that is, they permit of realizing perfectly the results which, according to Mannesmann, can be realized, but imperfectly, only by the use of solid cements.

As for the rest, as far as regards the mode of action of the various gaseous cements, the detailed explanations and the experimental data furnished in the first part of this volume are amply sufficient for the choice of the cement and of the conditions of operation which are best suited to obtaining definite results.

§ 5. CEMENTATION WITH MIXED CEMENTS

By "mixed cement" is meant a cement resulting from the simultaneous action of two or more cements belonging to two or more of the classes dealt with in the preceding sections.

For example, some of the liquid cements applied as "varnishes" may in a certain way be considered as mixed cements, and especially those in which, besides the fusible salt, there is present (or is formed during the heating) free carbon, which exercises its specific carburizing action in addition to that of the fused salt, though remaining, naturally, in the solid state.

But the only mixed cements which up to the present have found real technical applications on a large scale are those constituted of a solid cement and a gaseous cement, and especially those in which the gaseous carburizing constituent is formed exclusively, or at least mostly, of carbon monoxide. The first part of this volume contains complete data on their mode of action, and interesting practical results which their proper use makes possible. We also indicated there the lines along which, by suitably modifying the conditions of the operation, it is possible to make the characteristics of the cemented zones vary with certainty as desired within very wide limits.

The principal facts just referred to may be summarized as follows:

1. In cementation carried out with solid cements having carbon as their base, the carburizing action exercised on the iron *directly* by the free carbon, by simple contact and without the intervention of gaseous carburizing compounds, is very slight and in any case entirely negligible in industrial practice. This observation, as we have already seen, has been fully confirmed by the more recent researches of Guillet and Griffith,[1] of Weyl[2] and of Charpy;[3] the last scientist even returns to the conclusion, already drawn by others, that the *direct* carburizing action of carbon, in cementation with solid cements, is entirely *null*.

2. In cementation carried out with the solid cements ordinarily used in practice, the *specific* action of nitrogen (assumed and explained in various

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[1] See p. 122.

[2] See p. 124.

[3] See p. 124.

ways by many experimenters) is *very slight.* Only in cements containing large proportions of cyanogen compounds (alkali cyanides, ferrocyanides, etc.) does the direct action of volatile nitrogenous compounds occur to an appreciable degree.

3. In the cementations carried out with the solid cements ordinarily used industrially, the *direct specific* carburizing action of carbon monoxide is enormously preponderant over every other carburizing action.

4. Pure carbon monoxide cements iron at all temperatures between 700°–1300° C. at which cementation can be effected by any other cement. In fact, the velocity of the cementation (meaning the *depth* reached in a given time by the carburized zone), when working under suitable conditions, is, all other conditions being equal, greatest with carbon monoxide or a mixture in which carbon monoxide can exercise its maximum specific carburizing action.

5. The specific carburizing action which carbon monoxide exerts on iron at a high temperature is due to a series of chemical reactions whose course and states of equilibrium are at present known with precision. Moreover, the conditions of equilibrium of the systems in which these reactions are effected are in general comprised within the intervals of temperature and pressure ordinarily used in industrial practice. As a consequence it is possible to obtain a predetermined result with full certainty by using cements whose activity is due, if not exclusively at least mostly, to the specific carburizing action of carbon monoxide. It is even possible to thus obtain cemented zones in which the concentration of the carbon does not exceed a pre-established maximum limit and varies in a well-defined manner in the various layers of the zone. These definite results, variable at will within quite wide limits, are obtained by varying, according to definite rules, the temperature at which the cementation is effected, the pressure of the carburizing gas and the quantity of the carbon monoxide which in a given time comes in contact with unit surface of the iron or steel.

6. The results which are obtained by using carbon monoxide as cement vary in a well-defined way, all other conditions being equal, with variations in the chemical composition of the metal subjected to the cementation.

7. It is possible to vary the characteristics of the product in a well-defined way and within wider limits by using with the carbon monoxide substances capable of modifying the conditions of equilibrium of the existing chemical systems. These may be gases such as the hydrocarbons, nitrogen, etc., or solids such as carbon in its various forms. They can be made to act together with the carbon monoxide during the whole cementation, or only during a part of it.

8. The cements whose action is due to the specific carburizing action of carbon monoxide permit of obtaining with ease and certainty, with any kind of iron or steel, "mild" or "gradual" cementations, or "cemented zones of the intermediate type," in which the concentration of the carbon is low in the

external layers and decreases slowly and continuously in the successive deeper layers. This is the essential condition for avoiding the dangerous phenomena of brittleness and of "exfoliation" which show so frequently in steel objects cemented by the ordinary industrial processes.

9. The chemical reactions to which the carburizing action of the cements in which the active element is cyanogen is due are at present known only imperfectly, especially as regards their conditions of equilibrium, on which will depend the concentration of the carbon in the cemented zones. It is certain, however, that under practical conditions the states of equilibrium just referred to are strongly displaced in the direction corresponding to high concentration of the carbon passing into solution in the γ-iron. It results that the cyanides, the ferrocyanides and other derivatives of cyanogen, when used alone as cements, always give too "sudden" cementation, or cemented zones in which the concentration of the carbon is excessively high in an external layer of definite thickness and then suddenly and greatly decreases in the next layer beneath. Zones of this type give rise to dangerous phenomena of brittleness and "exfoliation" in the hardened product.

10. The gaseous or volatile hydrocarbons also, when used alone as cements, give too "sudden" cementations. The reasons for this are identical to those for the cements whose action is due to cyanogen or its derivatives.

The experimental proofs and the theoretical explanations of all the above ten statements are given and discussed in the first part of this volume.

On the basis of the facts above given, it follows clearly that those cements should be used in practice whose activity is due, if not exclusively at least mostly, to the specific carburizing action of carbon monoxide. To obtain the best results with one of these cements, with the maximum certainty, it is necessary to satisfy the following fundamental conditions:

1. The chemical composition of the cement must be perfectly *definite* and known with precision.

2. The composition of the cement must be as *simple* as possible.

3. The reactions which take place during cementation, between the various constituents of the cement and between these and the iron or steel, must be simple and lead rapidly, under the conditions most easy to realize in practice, to well-defined states of equilibrium corresponding to definite concentrations of the carbon in the cemented zones. From the theoretical point of view, the cement which best satisfies these conditions is carbon monoxide.

Nevertheless, the concentrations of the carbon in the cemented zones which correspond to the conditions of equilibrium with pure carbon monoxide are in general too low when working within the intervals of temperature and pressure ordinarily desirable to keep to in practice, and when the metal subjected to the cementation is an ordinary carbon soft steel or a steel of low nickel or chromium content. These disadvantages are not presented when using with the carbon monoxide, during the whole operation or during only a part of it, small and well-defined quantities of hydrocarbons or of solid carbon in a definite state of division. Such mixtures fulfill quite well the three conditions indicated above. The cements based on the simultaneous use of free carbon and of carbon monoxide are those best adapted to the greater number of ordinary technical applications, since they combine maximum simplicity in the operations with maximum certainty of reaching perfectly definite results. The principal technical advantages of the "mixed cement" based on the simple simultaneous action of carbon and of carbon monoxide may be summarized as follows:

1. Great "velocity of penetration" of the carburized zone. This fact, although it is not, as many practitioners still believe, the *most important* item of a given cementation process, is certainly very advantageous for many self-evident economical and technical reasons.

2. Great uniformity in the distribution of the carbon in the cemented zones. This easily permits of reducing to a minimum the phenomena of exfoliation of the cemented and hardened pieces.

3. Possibility of regulating (either by "diluting" the carbon monoxide with nitrogen, by limiting the contact of the carbon with the surface of the steel, or, finally, by suitably varying the temperature of the cementation during the operation) the concentration of the carbon in the cemented zone in such a way as to keep it within the limits (varying according to the composition of the steel subjected to the cementation) best suited to obtaining at the same time maximum hardness and minimum brittleness in the carburized layer.

4. Possibility of establishing *a priori* with full certainity the conditions necessary for obtaining a definite result, which can be chosen within quite wide limits and can be obtained with great precision.

5. *Continuous* use of the same carburizing materials (carbon and carbon monoxide), which never become "exhausted" but can be entirely utilized. This permits also of obtaining cementations of any depth whatever, without its being ever necessary to "renovate" the cement.

6. Absolute certainty of not introducing into the steel any foreign substance other than carbon, a condition which does not occur with the greater part of the cementation powders usually employed, containing organic nitrogenous substances, alkali cyanides, ferrocyanides, etc. This presents very great advantages in many cases.

7. Ease in keeping the surface of cemented pieces perfectly unaltered. In many cases this may be most useful, permitting of even dispensing with mechanical work upon the cemented pieces.

8. Possibility of reducing to a minimum the deformations and the variations in volume which the steel pieces undergo as the result of cementation,

and, in any case, the possibility of determining with precision *a priori* the variations in volume just referred to.

9. Ease in obtaining a good "protection" of the parts of the steel pieces which it is not desired to cement.

We have seen in the first part of this volume that normal cementation extends to a small distance from the parts of the metallic surface in contact with the granular carbon, even when the gas can circulate around the pieces with the greatest freedom, and that experiment shows that this distance becomes exceedingly small when the gaseous carburizing mixture ($CO + CO_2$) can circulate around the parts not in contact with carbon only through small channels, opposing considerable resistance to its flow. This is the reason that, working with the mixed cement, efficient "protection" of parts not to be cemented can be obtained when using protecting substances not altogether impermeable to gases, such as lean refractory clay, deposits of copper obtained by "dipping," loose covers of sheet metal, etc.

The form of furnace which, in general, is best suited to the industrial working of the process with which we are now dealing is that with vertical muffles, in which the pieces to be cemented and the solid cement are introduced successively above, while the gas is admitted below. The desirability of such an arrangement was shown in the laboratory experiments on the study of the mixed cement, which were described in the first part of this volume.

Nevertheless, it may at times be desirable to carry out cementation with mixed cement using an ordinary horizontal muffle furnace of the type described in the preceding pages. This may occur especially in two cases: First, when a large equipment of ordinary cementation furnaces with horizontal muffles would be an obstacle to the setting up of new special furnaces. Second, in the quite frequent cases where the pieces to be cemented have special forms, for which it appears, *a priori*, to be advantageous to work in horizontal furnaces.

While, therefore, the vertical muffle furnace presents very great advantages in those cases, most frequent in practice, in which the surfaces to be cemented are surfaces of revolution as, for example, gear-wheels, whether conical or cylindrical, axles, ball-bearing rings, the great majority of ordinary cutting tools, etc., yet the horizontal furnace, on the other hand, may be usefully employed in the less frequent cases of a different nature, for example, in the cementation of rails, sectors, etc.

The apparatus which is best adapted to this purpose will now be briefly described.

Since the gaseous current (ascending or descending) should traverse a layer of heated carbon of sufficient thickness (in general, at least 8–12 cm.) before enveloping the objects, the process with which we are dealing is possible only in furnaces holding rather tall muffles.

The muffle reproduced in the accompanying drawings must be considered as the lowest which can be practically used. The use of lower muffles would hinder the operations of charging, discharging, etc., while they would be facilitated by the use of muffles having a height even twice that shown. A greater height of the muffle also permits more advantageous proportions to be given to the various parts of the apparatus.

The cementation chamber consists of a retort of cast mild steel, of such form and dimensions that it can be placed inside the muffle of the furnace which it is desired to use. It should fit well, but in such a way that there is at least a centimeter between the upper wall of the retort and the arch of the muffle. Fig. 97 on p. 245 shows exactly the position occupied by the retort in the muffle, in an ordinary gas furnace with natural draft, made by Fletcher, Russell and Co. of Warrington.

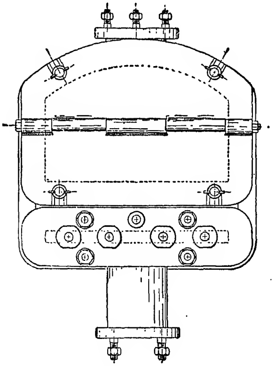

FIG. 132.

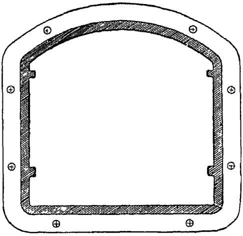

FIG. 133.

As is always advisable in such cases, the preservation of the muffle of refractory material is favored by ensuring that the retort should not be in direct contact with the muffle; this is obtained by interposing between the two, and especially on the floor of the muffle, a layer of refractory clay.

Two pairs of parallel rails, whose form and position are shown clearly in Fig. 133 (transverse section of the retort) and in Fig. 134, are fused on the inside lateral walls of the retort.

An "extension" or "head" of cast iron, shown in longitudinal section in Fig. 134, together with the retort connected with it, is fixed by means of eight set screws and nuts to the flange of the retort, which projects several centimeters from the furnace. This extension carries two channels designed for the charging and discharging of the granular carbon, and two openings, closed by covers fixed with set screws and nuts, as shown in Fig. 132, from the front, with the covers in position.

The cover which closes the upper larger opening is in two parts, connected by hinges, as seen in Fig. 134; this connection is so made as to be easily rendered impermeable to gases by placing a simple layer of the usual packing employed for boilers or steam cylinders. Other similar packings secure the tightness of the two covers set on the extension, and of the connection between the extension and the retort.

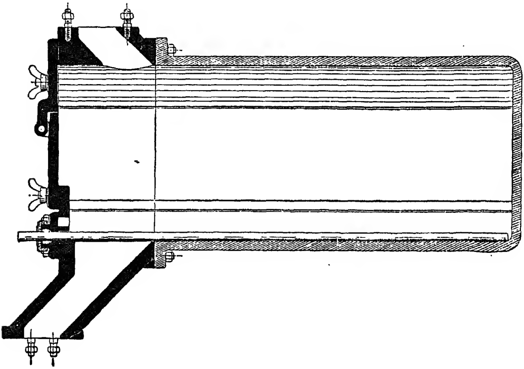

FIG. 134.

Through the lower cover, and by means of stuffing boxes (Figs. 133 and 134), there pass into the retort two iron tubes provided inside the retort with holes about 1 mm. in diameter every 2 cm.

The two closing apparatus represented in Figs. 135, 136, 137 and 138 are fixed with set screws and nuts to the external openings of the channels. Figs. 135 and 136 show the longitudinal section and plan of the closing apparatus which is to be applied to the upper channel of the extension. It consists simply of a steel muff, fixed at one end to a disk which permits of connecting it gas-tight to the channel of the extension, and closed at the other end with a hinged cover. In the wall of the muff, moreover, is inserted a side tube for the exit of the gases from the retort.

The second apparatus, shown in Figs. 137 and 138, consists simply of a steel draw valve to be applied, as in Fig. 137, to the bottom of the lower channel of the cast-iron head of the muffle. The draw can be pressed against the flange of the channel by means of a screw and stirrup, so that, with the aid of a disk of packing, it is easy to make it properly gas-tight.

The dimensions of the individual parts of the apparatus follow with sufficient precision from the drawings, on each of which is indicated the scale of reduction.[1] A good choice of the proportions of the various parts, and especially of those through which the granular carbon must pass, has great importance for successful operation. Only an exact knowledge of the physical properties of the granular carbon of various "gradations," acquired after long practice and many unsuccessful trials, has established the proportions indicated in the accompanying figures as best for the special case we are examining.

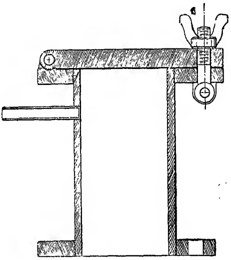

FIG. 135.—Scale 1/3.5.

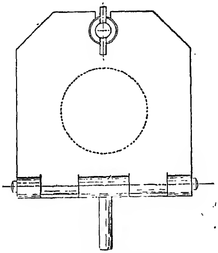

FIG. 136.—Scale 1/3.5.

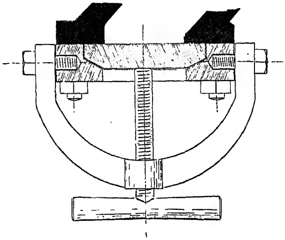

FIG. 137.—Scale 1/3.5.

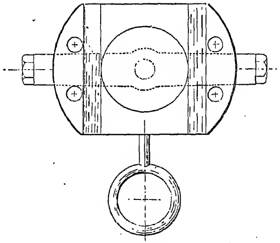

FIG. 138.—Scale 1/3.5.

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[1] The scales of the drawings here reproduced do not coincide with those usually adopted, because these drawings (made on a considerably larger scale) were reduced by a photomechanical process.

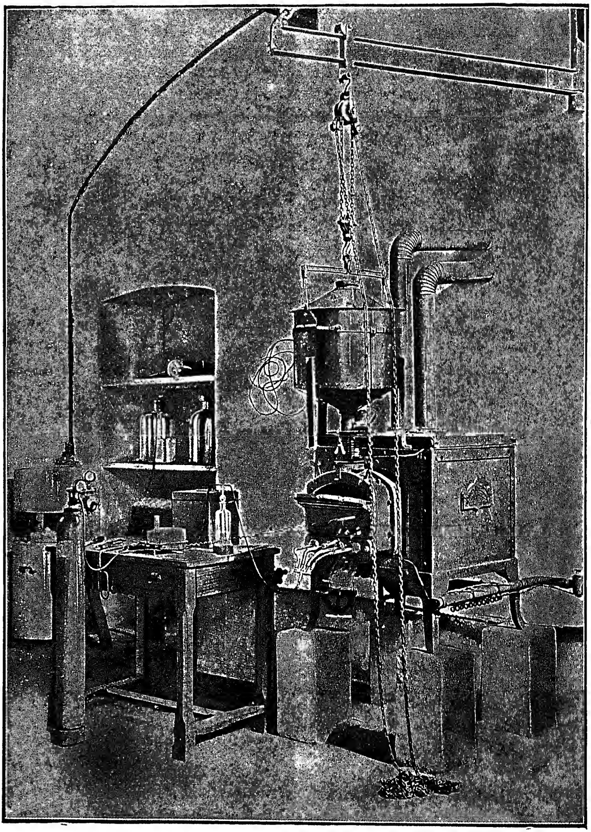

FIG. 139.

The various pieces described, connected in the manner indicated, constitute the whole furnace, shown with other accessories in Fig. 139.

As to the manipulation of the furnace, first of all a rectangular iron frame of slightly smaller dimensions is placed in the retort. This frame, consisting of a framework of T-iron on which is woven a net of iron wire with meshes about 10 mm., is placed in the retort in a horizontal position, resting on the two rails of the retort (see Fig. 133). Its purpose is to prevent the pieces approaching too close to the openings for the admission of gases. Having then closed the lower valve, the front lower cover and the lower half of the larger cover, the cover of the muff placed on the upper channel of the head of the retort is opened, and the lower exit tube of the receptacle which contains the granular carbon is introduced into the muff itself. This last receptacle, of sheet steel, is shown in section in Fig. 140, which requires no explanation. It is easily manipulated by suspending it by tackle, as shown in Fig. 139.

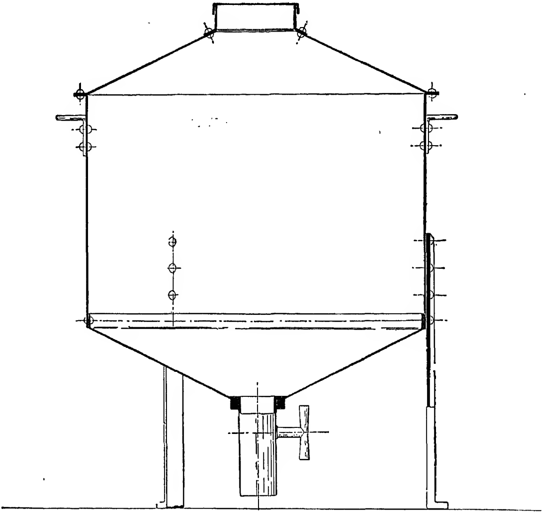

FIG. 140.

At the moment of beginning the charging, the apparatus is arranged just as shown in Fig. 139.

In practice, considering the short time between the charging of the furnace and the succeeding discharge, the granular carbon contained in the bucket can be at a high temperature. This is a point of great practical importance.

On gradually opening the butterfly valve which closes the lower opening of the bucket (see Fig. 140), there falls into the retort a certain quantity of granular carbon. This is rapidly spread over the bottom by the aid of an iron rake introduced through the upper half of the larger cover, so as to form a uniform layer reaching 4 or 5 cm. above the wire frame.

There is then placed on this first layer of carbon a second frame, like the first, on which are arranged, so as not to touch each other, the pieces which are to be cemented. On again opening the butterfly valve, fresh carbon falls into the retort and is uniformly distributed over the pieces by use of the rake. This operation is easier when the rake has two lateral projections which run on the two upper rails of the retort (Fig. 133). When the two projections are so placed as to keep the rake at such a height that it can not touch the pieces to be cemented, it is only necessary to run the rake rapidly from one end of the retort to the other while the carbon is being dropped in for it to fill all the interstices between the pieces of steel and to arrange itself in a uniform layer over them.[1]

If the pieces to be cemented are small, the operation can be repeated by placing a second series on the layer of carbon which covers the first.

If we have larger pieces or pieces of very elongated form which must be placed in the retort longitudinally, in a horizontal position, we can do away with the use of the third or even of the second frame, by placing the pieces directly on the second or on the first layer of carbon.

When the pieces are very large, it may be necessary to entirely remove the larger front cover of the head of the retort, so as to be able to introduce them. It is better to charge them only after having placed the first layer of carbon, and then it is necessary to put the cover in place, leaving only the upper half open to finish filling the retort.

All the pieces to be cemented having been placed in the retort, it is necessary to complete the filling with carbon. This is easily done by slowly dropping the carbon from the bucket into the retort and pushing it toward the end by means of the rake resting with its lateral projections on the two rails.

The operation is facilitated if the "blade" of the rake is fixed to the handle with a hinge such as to keep it perpendicular to the handle when pushed toward the end of the retort, but leaving it free to turn 90° when the handle is withdrawn. It greatly facilitates the final filling of the retort, especially when the pieces placed in it are of large dimensions and of irregular forms, to place in the retort a kind of hopper of sheet iron of elongated form, supported on the two rails by means of lateral extensions. When the hopper (which has about the form of a plane slightly inclined toward the end of the retort) has been pushed until it touches the end of the retort, the carbon is slowly dropped on the front end. As the carbon accumulates on the front end of the hopper, it is pushed, by means of the rake, along the surface of the hopper toward its other end, dropping it from here into the retort. If the hopper is gradually withdrawn at the same time, it is easy to completely fill the retort. This operation is naturally easier the higher the retort.

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[1] If the retort is taller, this operation can be made easier by placing the two rails at a greater distance from the pieces to be cemented.

The operation being finished, the upper half of the larger door of the retort is closed; then there is dropped into the retort through the butterfly valve the small quantity of carbon which is still necessary to fill the last space near the front door. Finally the butterfly valve is closed, the carbon hopper is removed, and the door of the upper muff, through which the carbon has been introduced, is closed.

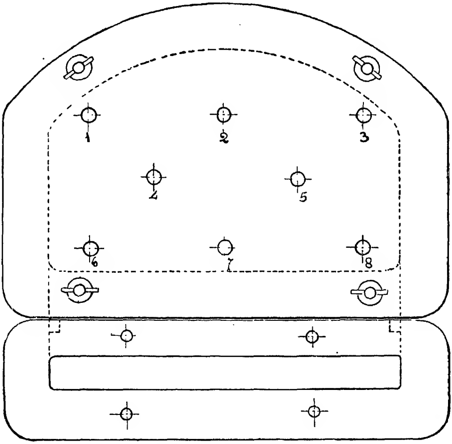

Fig. 141.—Scale, 1/5.

With a furnace of the dimensions and form shown in the accompanying figures, *the total time for the complete charging* of the furnace as just described varies *from six to eight minutes.* .

The retort having been charged and closed, there is admitted, by means of the iron tubes connected to its floor (see Fig. 134), a slow current of dry carbon dioxide so regulated that for every square decimeter of surface of steel to be cemented there circulates through the apparatus from 2 to 3 liters of carbon dioxide every hour. The gases issue by means of the tube fixed laterally to the upper muff (see Fig. 135), and may be collected in a gasometer, to be used again.

At the same time the furnace is lighted. It is well to give some precise data as to the course of the heating of the materials in the retort, for the comparison of these with those obtained when charging materials already heated will show the great advantages which can be obtained by working in this latter way. These data as a whole also present great interest as rules for regulating the time of heating in cementation carried out with solid cements in the ordinary boxes, since the specific heats and the thermal conductivities of the solid cements usually employed in practice are but slightly different from those of the "granular" wood charcoal to which the data about to be given refer.

Since the pieces to be cemented, together with the granular carbon, are placed in the upper half of the retort, the upper door of the retort (Fig. 132) was replaced by a sheet-iron plate of the same form, pierced by eight holes each about 10 mm. in diameter, distributed as shown in Fig. 141.

Iron tubes passed through these holes, extending to the back end, and closed inside with iron plugs. Having filled the retort with granular carbon, it was easy to follow the rise in the temperature in the various zones of this carbon by means of a thermo-electric couple (protected by porcelain tubes), whose junction was successively placed in various positions inside the iron tubes.

We give the results of two of many determinations thus carried out. The first was carried out with heating gas under higher pressure; the heating was therefore more rapid and the irregularities in temperature at the various points of the mass more marked.

The temperatures indicated below refer to points on a transverse plane section of the retort 20 cm. from the far end. The various points of this section are designated by numbers corresponding to those shown in Fig. 141.

EXPERIMENT I

(*a*) One hour after lighting the furnace

Region	Temperature	Region	Temperature
1	680° C.	5	580° C.
2	400° C.	6	570° C.
3	670° C.	7	less than 300° C
4	330° C.	8	320° C.

(*b*) Two hours after lighting the furnace

Region	Temperature	Region	Temperature
1	940° C.	5	580° C.
2	800° C.	6	600° C.
3	960° C.	7	300° C.
4	670° C.	8	520° C.

(*c*) Three hours and twenty minutes after lighting the furnace.

Region	Temperature	Region	Temperature
1	990° C.	5	1000° C.
2	990° C.	6	1010° C.
3	990° C.	7	1000° C.
4	1000° C.	8	1000° C.

EXPERIMENT II

(*a*) One hour after lighting the furnace

Region	Temperature	Region	Temperature
1	less than 300° C.	5	less than 300° C.
2	less than 300° C.	6	less than 300° C.
3	less than 300° C.	7	less than 300° C.
4	less than 300° C.	8	less than 300° C.

(*b*) Two hours after lighting the furnace

Region	Temperature	Region	Temperature
1	500° C.	5	450° C.
2	500° C.	6	480° C.
3	520° C.	7	420° C.
4	480° C.	8	420° C.

(*c*) Four hours and ten minutes after lighting the furnace

Region	Temperature	Region	Temperature
1	1000° C.	5	1000° C.
2	1000° C.	6	1030° C.
3	1000° C.	7	1000° C.
4	1000° C.	8	990° C.

From the data reported in the preceding tables, it follows most clearly that when the heating of the furnace is pushed rapidly, very great inequalities in temperature manifest themselves between various parts of the cementation chamber, which disappear (at least partially) only when the furnace has remained for a sufficiently long time at a high temperature. Now, the results of many experiments have shown that it is precisely these inequalities in temperature, manifesting themselves to an even greater degree in the usual cementation boxes filled with the ordinary solid cements, that are the principal cause of the great deformations which pieces subjected to ordinary cementation show.

If it is sought to avoid these inequalities in temperature by heating more slowly (as in the second experiment), we fall into the other disadvantage, which is practically a very serious one, of greatly prolonging the time of the cementation. And, moreover, as is seen from the figures, we succeed thus in diminishing only the extent of these inequalities in temperature, but not in entirely eliminating them.

The suitable temperature (900–1100° C.) having been reached, it is kept constant, being determined by a thermo-electric couple introduced from time to time into the retort through two or three openings made at suitable places in the covers and provided with iron tubes like those described in the above experiments.

In Fig. 132 one of these openings is shown in the lower cover. In Fig. 139 two are seen; in one of these (that near one side of the large upper door) is seen the thermo-electric couple, connected with the millivolt-meter.

The cementation having been finished, the screw which presses the slide of the lower opening of the head of the retort (Figs. 137, 138) is loosened, the stirrup which holds this screw is thrown aside, the hopper for the carbon (Fig. 140) is placed under the slide and the latter is opened by pulling the ring fixed in it. In this way, in less than two minutes, there passes from the retort into the receptacle beneath enough carbon to leave the cemented pieces wholly uncovered. The upper half of the larger door of the retort is then opened, or, if the cemented pieces are large, the door itself is removed directly, after first having opened the upper half. In carrying out this operation, the workman must take care to remain at one side of the apparatus, for when the upper half of the door is lowered air penetrates into the retort and forms with the carbon monoxide contained in it a combustible gaseous mixture which ignites and burns.

Having thus opened the retort, the cemented pieces are removed from it and it is at once charged again, using the still hot carbon collected in the hopper.

The removal of the cemented pieces takes, in general, less than two or three minutes, for only when they are of large dimensions and therefore few in number are they removed one by one. In case the pieces are small and numerous they are all removed together from the retort by simply removing the frame on which they were placed. On the whole, an operator who has acquired some practice in the manipulation of the apparatus can easily carry out all the operations for the complete discharging and recharging of the furnace in not more than ten or twelve minutes.

The interval between the dropping of the carbon from the retort and the charging of the same carbon again into the retort, for the successive charge, is hardly sufficient to produce any appreciable cooling of the carbon. Only a layer a couple of centimeters thick which comes in contact with the cold wall of the sheet-iron receptacle is decidedly cooled; the rest of the granular mass, protected by this external zone, which is a poor conductor of heat, does not appreciably cool. This causes the quantity of heat yielded by the granular carbon to the walls of the hopper to be small, so that the average temperature of the mass of granular carbon is not markedly lowered.

Accurate measurements made on the apparatus reproduced in the accompanying figures have shown that the carbon discharged from the retort at a temperature of 1000° C. can be replaced in it for the succeeding charge at a temperature of about 800°–900° C.

If we take into account the fact that only about half of the carbon contained in the retort is removed during the discharge, it is seen that the quantity of heat subtracted from the apparatus, besides that which is necessarily subtracted by the cemented pieces, is very much less than that which is lost in the ordinary processes of cementation, in which not only the cement and the pieces to be cemented but also the cementation boxes are charged cold into the furnace. The immediate consequence of this circumstance is the great rapidity with which the temperature of cementation is reached in the second and all succeeding charges. Thus, in a long series of experiments, cementing at 1000° C. with the furnace represented in Fig. 139, and keeping the pressure of the gas as in the second experiment cited above (in which, starting from the cold charge, the uniform temperature of 1000° C. was reached only after four hours and ten minutes) and recharging the granular carbon at a temperature of between 850° and 900° C. onto the new pieces to be cemented, placed *cold* in the retort, the uniform temperature of 1000° C. was again reached, on an average, in about twenty minutes after closing the retort.

When it is considered that the mean duration of a cementation of the depth usually adopted for machine pieces (0.5 mm. to 1 mm.) does not exceed two hours by this process, even when working below 900° C., and that a total of thirty to thirty-two minutes only is necessary to charge and discharge the furnace and to bring back the temperature to that suitable for cementation, it is evident that more than nine operations can be carried out in twenty-four hours in a small furnace like the one in question. The same furnace would give not more than two runs in the same time and with an equal consumption of fuel, when working with the ordinary cements and with the usual boxes.

If in addition we consider the economy of the cement and the much smaller wear of the fixed retort as compared with that of boxes which must be removed from the furnace at every operation, the great advantages of the new process are still more evident.

The possibility of charging the cement hot, has, besides its marked economical advantage, a great technical advantage, for it eliminates almost completely those inequalities in temperature which manifest themselves especially during the first period, when the cement is introduced cold into the furnace. Such inequalities are the principal cause of the deformations which the metallic pieces undergo during cementation. Every one who has carried out cementation industrially knows how serious and harmful, and often irreparable, are the effects of these deformations.

Besides this, the lack of uniformity in temperature of the materials contained in the cementation boxes in the ordinary processes, even if limited to a part of the total time of the operation, is the cause of great irregularities in the cemented zones, in which the depth and the concentration of the carbon undergo great variations between one point and another.

The uniformity in temperature during the period which precedes the attainment of the constant temperature of cementation is still more perfect if, besides the solid cement, the pieces to be cemented are also first preheated to the temperature of cementation and placed in the retort at this temperature. In this case the time necessary to reach normal temperature of cementation after charging is shortened still more. Thus, by working under the same conditions as indicated above but charging the pieces of steel heated to about 800°–850° C., this time is reduced from twenty minutes to only ten minutes.

Of all the parts which I have described, the only one which must be renewed rather frequently is the horizontal frame placed within the retort. Of this, the metallic net can serve for four or five operations, but its cost is negligible. The frame can, on the contrary, serve for a far larger number of cementations. The retort not having to be removed from the furnace for the operations of charging and discharging, lasts much longer (from thirty to forty times longer, and even more) than ordinary boxes which are removed from the furnace, while for an equal capacity it costs about the same. All the other parts have a practically unlimited duration.

There follow some concrete data on the results which can be obtained with the process just described.

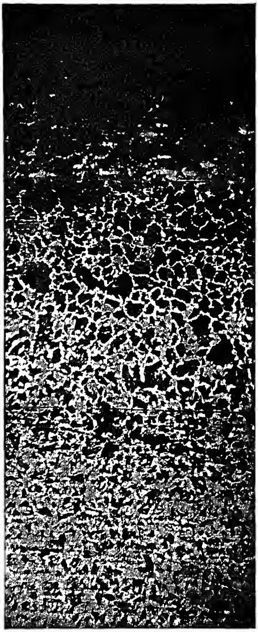

FIG. 142.

As regards the velocity of cementation, the concentration and distribution of the carbon, and other "local" characterististics of the cemented zones which are obtained, the observations already noted in the first part of this volume, in connection with work in vertical cementation chambers, hold unchanged.

Fig. 142 shows, enlarged 50 diameters, a microphotograph of a section of a carburized zone, etched with picric acid in 5% alcoholic solution. This was obtained by cementing a soft steel for two hours at 1000° C. by the process described in the preceding pages. The micrograph shows clearly all the characteristics of those zones which I have called of "intermediate type," such as maximum concentration of the carbon 0.9%, the gradual decrease in this concentration, etc. These were studied and their marked practical advantages demonstrated in the first part of this volume.

The manner in which the cementation distributes itself over the whole surface of pieces of iron or steel charged into the retort is of practical importance. This distribution will be perfectly uniform, whatever may be the form of the pieces to be cemented, provided some simple conditions are realized. When these conditions are fulfilled, we may be certain *a priori* that the cementation will be perfectly uniform and that there will not be formed such non-carburized or slightly carburized or highly carburized "regions" which are so frequently formed with the ordinary solid cements, as the result of variations in the contact of the cement with various parts of the surface of the pieces.

First of all, it is obviously necessary that the temperature of the pieces should be as uniform as possible during the whole time of cementation. We have seen that this condition is easily met in the process with which we are dealing, especially when, besides charging hot carbon, the pieces to be cemented are also charged hot. In the second place, the state of the "granular" carbon used has great influence on the uniformity of the cementation. It is necessary, in fact, that the gases should be able to circulate with the same ease through all parts of the retort. This can be obtained with certainty only by using carbon in uniform sized grains. In general, for the cementation of pieces of the usual form (gear wheels of medium dimensions, drills, etc.), the best results are obtained by using ground wood charcoal and discarding the portions which pass through a sieve of 64 mesh per sq. cm. and which are retained by a sieve of 16 mesh per sq. cm.

In the third place, in order that the cemented zones may be uniform throughout their whole extent it is necessary that the gaseous mixture of carbon dioxide and monoxide should have already attained completely to chemical equilibrium with the carbon by the time that it reaches the nearest points of the objects to be cemented. This is attained by working with a sufficiently slow current of gas and by making it pass through a sufficiently thick layer of carbon before it reaches the pieces to be cemented. Experience indicates that the velocity of the gaseous current and the thickness of the layer of carbon must be regulated according to the temperature, the nature of the metal to be cemented, etc. If ordinary soft steels are to be cemented at temperatures near 1000°, under the conditions described in the preceding pages, the special data reported above apply best, both as regards the velocity of the current of carbon dioxide and the thickness of the layer of carbon.[1]

If the velocity of the current of carbon dioxide is too high or the layer of carbon through which it must pass before reaching the pieces of steel is too thin, the cemented zone will not be uniform, showing a minimum of thickness and of concentration of carbon near to the points where the gas arrives.

For cementing with the mixed cement of carbon and carbon monoxide whenever the pieces do not specially require the use of a horizontal furnace, it is by far preferable to use furnaces with vertical muffles of the type already described (p. 294) for cementation with gaseous cements. In fact, that particular furnace was designed expressly for cementation with the mixed cement we are now considering.

Figures 130 and 131 and the accompanying description suffice for present purposes. The part of the operations constituting the cementation proper, such as the charging of the pieces, their removal for quenching, the control of the temperature and of the circulation of the gases, etc., is identical whether gaseous cement or the mixed cement is used. We will therefore give here a description of the operations of cementation carried out with mixed cement only where they begin to differ from the operations when gaseous cements are used. This is at the point when, the charging of the pieces to be cemented into the retort having been completed, the cement is introduced into the cementation chamber.

When the pieces to be cemented have been placed in the retort in the manner previously indicated (p. 296), the retort is covered; then, through the central opening of the latter, is passed the lower discharge tube of the sheet-iron receptacle *O* (see Fig. 130) full of still-hot granular carbon (in general, above 900° C.) discharged from the retort at the close of the preceding cementation.

Figure 143 shows how this operation is carried out. The receptacle *O* is easily manipulated above the muffles by suspending it with tackle to a revolving arm or to a light trolley.

The walls of the receptacles, even when filled with granular carbon at 1000°, are not heated higher than to 200°–250° C. during the time required for carrying out all the operations of charging and discharging the retorts, even when working under the most unfavorable conditions. This is easily explained by the small heat capacity and the low heat conductivity of the mass of "granular carbon," which, even if at a high temperature, can give to the walls of the receptacle which contains it but a small quantity of heat. This is easily dissipated by the simple cooling of the metallic wall by the current of air which envelops it.

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[1] If the retort which is used is tall, the first layer of carbon can be made thicker without cramping the space intended for the pieces of steel; this is always convenient and desirable.

The receptacle *O* having been placed in the manner just indicated, the butterfly valve which closes its lower end *N* is gradually opened, filling in a few seconds, with the hot granular carbon, all the free spaces in the retort between the pieces charged into it.

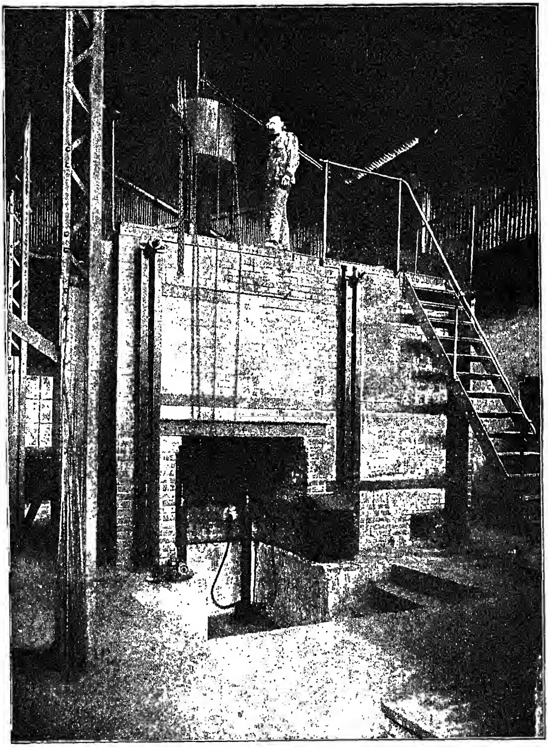

Fig. 143.

As to the form and dimensions of the various valves, the proper working of which is essential to the successful operation of the apparatus, they are the same as those described, with illustrations, in the case of furnaces with horizontal muffles.

The "granular" carbon used for cementation with the mixed cement possesses, especially at a high temperature, a mobility comparable to that of a liquid. This makes it capable of penetrating, by its own weight, into all the interstices between the objects to be cemented, and between them and the wall of the retort. It is also easy to assist the filling by means of iron rods introduced through holes in the cover of the retort, and manipulated by a workman who stands on the furnace.

Having introduced the granular carbon up to a level about 8 to 10 cm. lower than the upper edge of the retort, the butterfly valve of the tube *N* is closed, the receptacle *O* is raised, the central opening in the cover of the retort is closed, the plunger *L* is completely lowered, the tube *D* is screwed to the piece *C*, and through it is slowly admitted carbon monoxide or carbon dioxide, pure or mixed with air. This passes to the distributor *E* and thence to the retort.

An ordinary gas meter is used to regulate the current of carbon monoxide. This may be of the so-called "dry" type, and connected with a small anemometer, to measure the velocity of the gaseous current.

This done, the cementation proceeds at once, it being merely necessary to observe and regulate both the current of carbon monoxide and the temperature.

For observing the temperature, which is not frequently necessary with a furnace of the type described, when properly set in operation, an ordinary thermo-electric pyrometer is introduced from time to time at various parts of the granular carbon contained in the retort, by passing it through a few holes made in the retort cover. The temperature of operation must be kept perfectly constant at some definite value, chosen beforehand, usually between 900° and 1100° C. The gases which issue from the retort through the tube passing through the cover may be collected in a gasometer and used for succeeding cementations, after suitable treatment and correction of composition.

When the cementation has proceeded for a time suited to producing the desired results, which can be fixed with great precision *a priori*, the current of carbon monoxide is interrupted, the tube *D* is removed, and the discharging of the retort is begun.

When special results are not to be obtained, all of the granular carbon is directly removed from the retort by dropping it through the slide valve *Q* into the receptacle *O* placed beneath.

When, however, the specific action of the carbon monoxide must be "isolated" during the last phase of the cementation from the "direct" action of the granular carbon, in order to obtain exceptionally "gradual" cementations, the receptacle O is placed in such a way that the neck of the funnel B enters the uncovered tube P; then, by gradually opening the slide valve Q, there is drawn from the retort[1] such a quantity of granular carbon as to leave uncovered those parts of the objects in which it is desired to "graduate" the cementation, although there still remains enough in the retort to insure the desired conditions of chemical equilibrium in the gaseous mixture.

The total removal of the carbon from the retort is effected only when the second phase of the cementation, with "isolated" carbon monoxide, has been protracted sufficiently to obtain the desired results.

In both cases, when all the granular carbon has escaped from the retort, the cover is raised. In doing this, the workman must take care to remain at a safe distance from the upper opening of the retort, for the air which enters forms with the carbon monoxide in it a mixture which ignites quickly, because of the high temperature of the retort. This rapid ignition is not dangerous, but can be avoided by completely opening the retort before withdrawing the carbon, (in which case, however, some of the granular carbon burns), or by rapidly "sweeping out" the muffle with a little carbon dioxide after having removed all the carbon. It is necessary, however, that this operation should be carried out rapidly, so as to avoid the carbon dioxide producing some superficial decarburization of the cemented pieces.

When the pieces to be cemented are supported directly by the disk F, as, for example, when a "column" of gear wheels has been charged, the pieces may also be raised as far as the uncovered upper opening of the muffle without first expelling the granular carbon from the retort. This procedure has the disadvantage of making it less convenient to take away the pieces for quenching, and of burning a considerable quantity of the carbon contained in the retort.

Whether or not the carbon has been removed from the retort, when the cover R is opened, the plunger L is lifted until the terminal cone M fits into the hollow of the piece C, then the hydraulic cylinder I is kept slowly operating so as to gradually raise the carriers C, E, F with the cemented pieces on them. Then the removal and the quenching is begun, in the same manner as when a gaseous cement is used.

In placing the objects to be cemented in the retort very small pieces are placed in "cages" made of frames of iron rods joined by nets of iron wire and placed on successive layers of granular carbon. Pieces of small dimensions can also be placed free on successive layers of granular carbon. This permits of easily cementing even very small objects, for which we have seen (see p. 299) that this same furnace with vertical muffles is not well suited when it is used with gaseous cements.

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[1] The carbon contained in the retort escapes from it by first passing through a series of openings made in the base ring on which the parts C, E, F rest. These openings appear only in dotted lines in the accompanying drawing, owing to the way in which the section drawing was made.

As regards the time necessary, the length of these operations depends on the forms and dimensions and therefore on the number of the pieces to be cemented in a charge.

To cite some concrete data, when the charge was composed of some thirty cylindrical gear wheels forming a single "column" in the retort, the times were as follows:

(*a*) Placing of the objects to be cemented on the platform, one to two minutes.

(It is clear that the length of this operation is greater the smaller and the more numerous the pieces charged, but, even for very small pieces, placed free in layers alternating with layers of carbon, the most unfavorable case, it does not exceed, in general, five minutes.)

(*b*) Placing in position the cover of the retort and the receptacle containing the granular carbon..about one minute.

(*c*) Complete filling of the retort with the granular carbon, from one and one-half to two minutes.

(This operation also becomes somewhat longer when the pieces to be charged are very small and numerous. In general, however, even in the most unfavorable cases, it does not require more than four minutes.)

(*d*) Total lowering of the plunger of the hydraulic elevator, placing of the tube for the admission of the carbon monoxide, removal of the receptacle for the granular carbon and complete closing of the cover of the retort, in the aggregate, about one minute.

As is seen, in the case chosen as example, the aggregate duration of the operations necessary for the complete charging of the retort may vary from four and one-half to six minutes. In the other more unfavorable cases cited above, it may, on the contrary, reach ten to twelve minutes.

For the discharge the following approximate data hold:

(*a*) Removing the tube carrying the carbon monoxide, placing the receptacle for the granular carbon under the lower neck of the retort and opening of the draw valve.................in the aggregate, about one to one and one-half minutes.

(*b*) Passage of all of the granular carbon from the retort to the receptacle below, and closing of the draw valve..........from one and one-half to two minutes.

(*c*) Raising of the carrying platform and discharge of all the cemented objects...from one to two minutes.

(If the cemented objects are very small and very numerous and especially if they are placed free in layers on the carbon, this last operation may require up to ten minutes.)

In general, it may be considered that the complete discharge of the retort lasts from three and one-half to thirteen minutes. This duration may extend in the most unfavorable cases up to thirteen or fourteen minutes.

The cementation never exceeds two hours per batch, and is often only one hour, for almost all the cases occurring in the manufacture of cemented pieces for machine parts, in which it is seldom that cemented zones thicker than 2 mm. must be obtained. This is counting the time from when the charging of the retort is finished to when its discharging is begun, and, therefore, including the time necessary to reach the temperature of operation. The latter period is reduced to about ten minutes when the carbon and pieces are charged hot.

Under practical conditions a *complete* operation requires less than two hours and a half. The weight of the pieces which can be charged into the retorts shown in the accompanying furnace drawings varies from 100 kg. to over 500 kg. Each retort, therefore, will cement in twenty-four hours from one ton to about five tons of iron or steel objects.

Taking into account the reduced consumption of fuel which the furnace described attains, the very low cost of the cement and its being *totally* utilized without any waste, it is clearly seen that the process of cementation under consideration is highly economical.

Practice shows that this cost, when pieces of medium dimensions, from 100 grams to 10 kg., are cemented to a medium depth, is about one-fifth to one-tenth that of the same cementation carried out with Caron cement in the ordinary boxes.[1]

Aside from any consideration as to the superiorty of the product there are advantages of a technical order presented by the furnace with vertical muffles just described, when compared with the horizontal muffle furnace used for cementation with the mixed cement. These advantages consist

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[1] As a concrete example, it may be desirable to summarize briefly some data relative to the industrial cost (including, that is, interest, depreciation, general costs, etc.) of the cementation of machine pieces carried out in a furnace with vertical muffles of the type and of the dimensions described in the preceding pages.

The furnace costs about 20,000 lire ($4000), including the principal accessories, and produces from 1200 to 2400 kg. of cemented pieces per day. The daily costs of working, taken from the mean of a long operation, are as follows:

1. Retorts of sheet steel........................Lire	3.60	$0.70
2. Refractory muffles..........................	1.05	0.20
3. Solid cement..............................	1.44	0.28
4. Gaseous cement............................	0.90	0.17
5. Labor....................................	10.00	1.93
6. Fuel (including quenching)....................	28.00	5.40
7. Interest and depreciation charges on furnace and accessories..................................	18.00	3.48
8. General expenses (same as labor)...............	10.00	1.93
Total..................................Lire	72.99	$14.09

Referring this aggregate cost to the *minimum* daily production of the furnace (1200 kg) so as to obtain the *maximum cost* of the cementation, we reach a cost of 6.083 *centesimi* 1.174 *cents*) per kilogram (2.2 lb.) of pieces cemented to an average depth of 1 mm. (0.04 in.) and hardened.

essentially in the greater rapidity and simplicity of the operations, and in the greater uniformity of treatment of all the pieces constituting the charge, a uniformity which is not limited merely to the raising and maintaining of the temperatures but applies with greater force to the distribution of the carburizing gas.

In the vertical furnace, arranged as described, the "harmful spaces" which remain in the charged retort are reduced to a minimum. This does not occur in the horizontal muffle furnaces, in which these harmful spaces, representing losses of heat and of carburizing materials and greatly reducing the output of the furnace, are always present to a marked degree, especially in the "head" of the retorts.

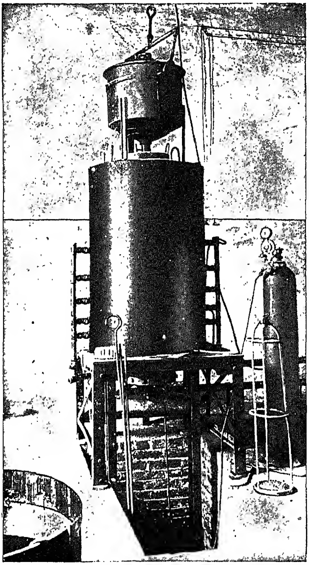

Fig. 144.

Finally, the vertical muffle furnace just described permits of carrying out with great ease, and without the addition of any new part, the cementation of the ends of pieces of very elongated form (such as connecting rods, shafts, etc.), while in ordinary cementation furnaces these results can be obtained only by adding to the furnace *special* parts, *different* from those in which the cementation of pieces of ordinary forms and dimensions are carried out.

The type of furnace described, with vertical muffles, is the best adapted to utilizing in the best way the advantages of the mixed cement, with carbon monoxide as base, either from the point of view of quality of the products, certainty of the results, or economy of production.

When only small quantities of materials are to be cemented, and especially when the operation is to intermittent, there is great advantage in using a vertical muffle furnace heated by illuminating gas, or even by heavy oil. This type has been already spoken of on p. 253 and is shown in Fig. 106.

All that has been said in the preceding pages for the gas-producer furnace holds for this furnace, both as regards its advantages over the horizontal muffle furnaces and as regards its working and the operations of charging and discharging. Fig. 144 shows an arrangement for filling with the hot granular carbon the spaces in the retort left free by the pieces charged into it.

With a small furnace of this type, whose useful space in the retort has a diameter of 28 cm. and a height of about 1 meter, and especially for intermittent operation, the cost of the cementation is somewhat higher than with the continuous gas-producer furnace. It does not often exceed, however, 12–15 centesimi (2.4–3.0 cents) per kilogram (2.2 lb.) of cemented pieces.

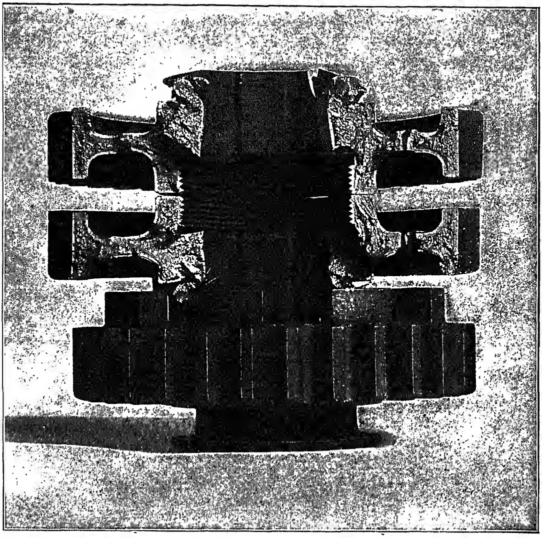

FIG. 145.

The characteristics of the cemented zones which are obtained by working under various conditions with the mixed cement having carbon monoxide as base have been already amply described in the first part of this volume.

There is reproduced in the accompanying figure (Fig. 145) the surface of fracture of a gear wheel cemented in the vertical muffle furnace with the mixed cement having carbon monoxide as base, then quenched and broken. In the wheel here shown no part was "protected," in order to show more clearly the homogeneity of the cementation throughout the entire surface.

The figure shows clearly how the mixed cement gives, even on pieces of complicated form, cemented zones of a uniformity equal to that of the zones obtained with the gaseous cements. Moreover, a comparison of this surface of fracture with those shown in Fig. 129 confirms very clearly the statement that the mixed cements with carbon monoxide as base permit of avoiding those sudden variations in the carburization, and therefore in the hardness, which characterize the cemented zones obtained with the ordinary mixed cements with hydrocarbons as base. Fig. 145 also shows that the harmful consequences of such sudden variations in the structure *viz.*, exfoliations, are also eliminated. In fact, the wheel shown in Fig. 145 has suffered strong deformation before breaking, but at no point has the least *exfoliation* shown itself.

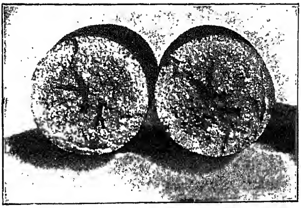

FIG. 146.

The same absence of sudden variations in structure is observed still better in the surfaces of fracture of cylinders cemented with the usual mixed cement, shown in Fig. 146, especially if these surfaces of fracture are compared with those shown in Fig. 129.

As regards the "velocity" of the cementation, a simple comparison of the data already cited proves the great advantages obtained by using the mixed cement with carbon monoxide as base. Thus, for example, compare the data reported on p. 135, relative to cementation with carbon monoxide and carbon, with those cited on p. 217, carried out with a mixture of wood charcoal and bone charcoal (Bildt), and with those cited on p. 272, carried out with four solid cements in common use (Grayson), and with many other data already cited in the first part of this volume.

We will add here a somewhat more extended account of a practical character concerning the modifications in the conduct of cementation with the mixed cement for the purpose of lowering the maximum carbon content in the cemented zones and rendering its distribution more uniform. This is especially important in the cementation of certain special steels.

The result just indicated can be obtained by modifying the conduct of the cementation along two lines, either by "diluting" the carbon monoxide used with an inert gas, or one almost inert, like nitrogen, or by "isolating" during a part or all of the cementation the action of the carbon monoxide from the simultaneous action of the carbon intended to "immediately regenerate" it. Very precise results can be obtained in practice with each of these two methods.

I have already pointed out before (p. 164) that in case the reactions which take place in the use of carbon monoxide and free carbon should lead to successive states of complete chemical equilibrium, the concentration of the carbon in the cemented zones ought not to depend in any way on the partial pressure (concentration) of the carburizing gaseous mixture (carbon monoxide and carbon dioxide taken together) with respect to the inert gases added. This is because, as Schenck has shown,[1] the isothermal pressure-composition curve for the mixtures of carbon dioxide and carbon monoxide in equilibrium with free carbon coincides throughout its whole length with one of the equilibrium curves of the same gaseous mixtures with the iron-carbon mixed crystals. This last curve (forming part of a pencil of curves, each corresponding to a given concentration of carbon in the mixed crystals) is just that one which determines the maximum concentration attainable by the carbon in the cemented zones obtained at a given temperature by the process now under consideration.

But it has been already pointed out (see p. 188) that in these processes true states of complete equilibrium can be reached only in the case (never realized practically) in which the operation has been protracted so long that the whole mass of the metal subjected to cementation is uniformly carburized.

In the contrary case (the only one which ordinarily occurs in practice), when the carburized zone is limited to a portion of the mass of the steel, a new coefficient modifies the final result; *viz.*, the *velocity* with which the gases and the carbon of the mixed crystals diffuse into the solid steel. The intervention of this new "velocity" coefficient causes the *absolute* velocity of the various reactions to also exercise an effect, which they could not exercise if states of complete equilibrium were reached. This affects the final result of the cementation, and especially the concentration of the carbon in the cemented zones. But since these absolute velocities vary with variations in the partial pressure (dilution or concentration) of the active gases, it can be foreseen that the variations in this partial pressure will produce practically utilizable variations in the concentration of the carbon in the cemented zones.

Many experimental results confirm the correctness of these remarks, and constitute concrete examples of the practical results which can be obtained by applying the principles to which I have referred.

To work with "diluted" active gases, it is sufficient to simply substitute air for the carbon dioxide, working otherwise in the same manner as indicated for cementation with carbon monoxide. It is clear that the mixture of active gas resulting from the action of oxygen of the air on the carbon will in this way be diluted with a volume of nitrogen about double its own volume,

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[1] See Schenck, *Chimie physique des métaux*, 1911, pp. 200–201 (translated by Lallement), Paris, Dunod et Pinat, 1911.

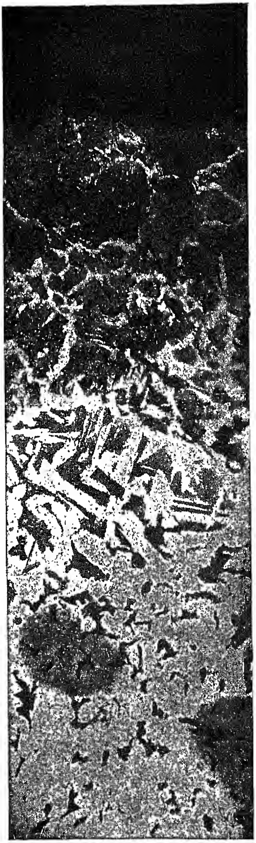

FIG. 147.

since, at the temperature of the cementation, the active mixture is composed almost wholly of carbon monoxide, containing but 1% or 2% of carbon dioxide.

Figs. 147, 148 and 149 show, magnified 50 diameters, sections etched with a 5% alcoholic solution of picric acid. They are three cemented zones obtained by making the carbon act in a slow current of air on an ordinary soft steel under conditions identical to those described in the preceding pages, and at the temperatures and during the times indicated.

FIG. 147.—Six hours at 1000° C.
FIG. 148.—Six hours at 1100° C.
FIG. 149.—Twelve hours at 1100° C.

A simple comparison with the micrographs shown in the first part of this volume, and also with Fig. 142, shows clearly that the dilution of the mixture of active gas ($CO + CO_2$) with an inert gas or one almost inert, such as nitrogen,[1] results in a marked decrease in the maximum concentration of the carbon in the cemented zones,[2] although there is preserved therein the characteristic uniform distribution of the carbon which constitutes the principal advantage of the process.

The practical advantages which can be obtained in many cases by the application of this last modification of the process with which we are dealing are

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[1] See F. Giolitti and L. Astorri, *Ricerche sulla fabbricazione dell'acciaio cementato*, IV (*Gazz. Chim. Ital.*, 1910, XL, I).

[2] From all the data reported previously we see that by working under the conditions giving the zones reproduced in Figs. 147, 148 and 149, there would have been obtained a maximum concentration of the carbon of at least 0.9% extending to a layer of a thickness equal to at least one-third the total thickness of the cemented zone.

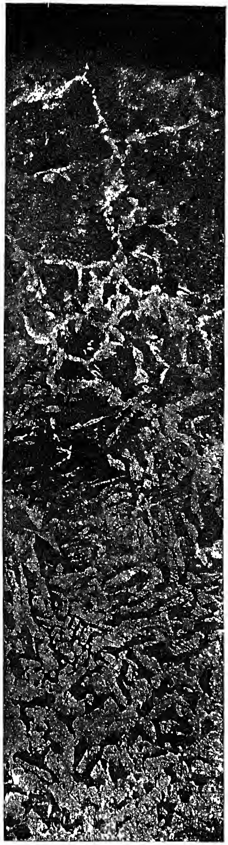

FIG. 148.

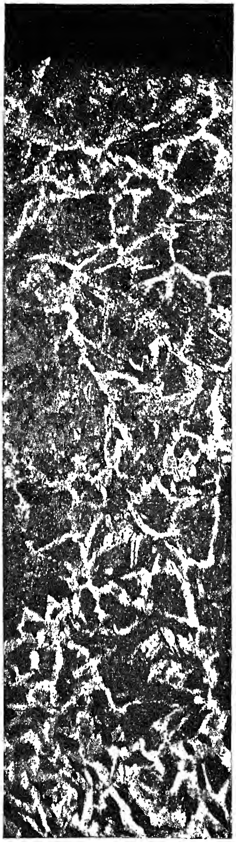

FIG. 149.

evident, especially in the cementation of those special steels for which the particular curve of equilibrium of the mixture of carbon dioxide and carbon monoxide with its mixed crystals coinciding with the curve of equilibrium of the same mixture with carbon corresponds to a rather high concentration of carbon in the mixed crystals.

Let us see, now, some practical examples of the results which can be obtained by the second method, consisting in isolating, during a part of the cementation, the action of the carbon monoxide from that of the free carbon, which we have already seen can easily be obtained with the vertical furnace by expelling at the suitable moment from the cementation chamber that portion of the granular carbon which in the first part of the operation was in direct contact with the surface of the objects to be cemented, and leaving in the lower part of the retort a layer of this carbon of sufficient thickness to establish the chemical equilibrium of the gaseous mixture which passes through it.

The effects of the isolated action of the carbon monoxide on the cemented zones obtained by the mixed cement acting in a first phase of the operation have already been referred to, especially on pages 135 to 137. But, while I dealt then with the effects to which such a procedure gives rise when it is applied to thin cemented zones, the data which I now wish to present refer to cementations of medium depth (from 5 to 10 mm.), for which (as also for the deeper ones) the application of the procedure in question presents the greater technical interest.

The tables which follow give the data (gravimetric carbon determinations in layers 0.5 mm. thick) of some cementations carried out with the mixed cement and followed by the action of the carbon monoxide, "isolated" in the way which I have indicated above. The same results are represented graphically in the diagrams which follow the tables of each series. The precise conditions under which the operation was conducted in its two distinct phases are also given.

Series I

Material used: ordinary soft steel of the following composition:

Carbon	0.12 percent.
Silicon	0.06 percent.
Manganese	0.47 percent.
Sulphur	0.02 percent.
Phosphorus	0.03 percent.

Results after each of the individual phases of the treatment:[1]

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[1] Both in this first series of experiments as also in the following series, several pieces of steel were subjected simultaneously to each of the various treatments, and under identical conditions, one of them being then used, after each operation, for the gravimetric determinations of the carbon in the successive layers.

(*a*) Cementation of ten hours at 1100° C. with mixed cement:

No. of individual layer analyzed	Distance of surface of the piece from the median zone of the layer analyzed (mm.)	Concentration of the carbon in the individual layers		
		1st determination	2nd determination	Mean
1	0.5	1.16	1.18	1.17
5	2.5	0.80	0.82	0.81
10	5.0	0.33	0.35	0.34

(*b*) Heating of the preceding zone for five hours at 1100° in "isolated" carbon monoxide:

No. of individual layer analyzed	Distance of surface of the piece from the median zone of the layer analyzed (mm.)	Concentration of the carbon in the individual layers		
		1st determination	2nd determination	Mean
1	0.5	0.84	0.86	0.85
5	2.5	0.76	0.80	0.78
10	5.0	0.46	0.46	0.46
15	7.5	0.23	0.27	0.25

(*c*) Heating of the preceding zone for another five hours (in all, ten hours of heating) at 1100° in "isolated" carbon monoxide:

No. of individual layer analyzed	Distance of surface of the piece from the median zone of the layer analyzed (mm.)	Concentration of the carbon in the individual layers		
		1st determination	2nd determination	Mean
1	0.5	0.69	0.71	0.70
5	2.5	0.66	0.68	0.67
10	5.0	0.52	0.54	0.53
15	7.5	0.38	0.40	0.39

The numerical data contained in the three tables constituting the first series are represented graphically in the following diagram (Fig. 150).

SERIES II

Material used: chromium-nickel steel of the following composition:[1]

Carbon..........	0.33 percent.	Phosphorus.....	0.015 percent.
Silicon..........	0.06 percent.	Chromium.....	1.50 percent.
Manganese......	1.15 percent.	Nickel.........	3.17 percent.
Sulphur.........	0.02 percent.		

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[1] As is seen, this is a steel of the type of the ordinary steel for Krupp armor. For it the data here reported, relative to cementations of slight depth, are certainly of interest. A greater interest, however, will be presented by the data (given later) of very deep cementations carried out on this steel with the process just described.

Results after each of the individual phases of the treatment:
(*a*) Cementation of ten hours at 1100° C. with the mixed cement:

No. of individual layer analyzed	Distance of surface of the piece from the median zone of the layer analyzed (mm.)	Concentration of the carbon in the individual layers		
		1st determination	2nd determination	Mean
1	0.5	1.18	1.14	1.16
5	2.5	0.79	0.82	0.81
10	5.0	0.49	0.51	0.50

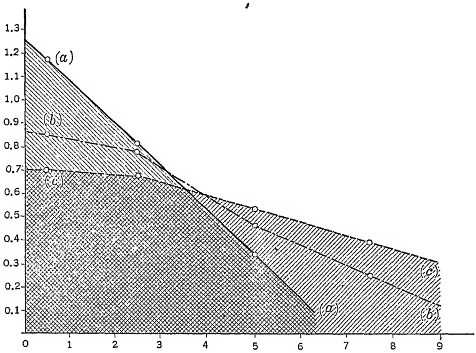

FIG. 150.

(*b*) Heating of the preceding zone for five hours at 1100° C. in "isolated" carbon monoxide:

No. of individual layer analyzed	Distance of surface of the piece from the median zone of the layer analyzed (mm.)	Concentration of the carbon in the individual layers		
		1st determination	2nd determination	Mean
1	0.5	0.80	0.81	0.80
5	2.5	0.76	0.78	0.77
10	5.0	0.58	0.58	0.58
15	7.5	0.45	0.44	0.45

(*c*) Heating of the preceding zone for another five hours (in all, ten hours of heating) at 1100° C. in "isolated" carbon monoxide:

No. of individual layer analyzed	Distance of surface of the piece from the median zone of the layer analyzed (mm.)	Concentration of the carbon in the individual layers		
		1st determination	2nd determination	Mean
1	0.5	0.87	0.85	0.86
5	2.5	0.85	0.88	0.87
10	5.0	0.75	0.75	0.75
15	7.5	0.60	0.58	0.59

The numerical data contained in the last three tables constituting the second series are represented graphically in the following diagram (Fig. 151).

After the detailed study in the first part of this volume on the causes of the various phenomena of brittleness and of exfoliation which may manifest themselves in cemented steels, any explanatory comment on the data contained in the preceding tables and represented in the two diagrams would be superfluous. In fact, when we remember the conclusions from those studies, a simple examination of the gradual variations in form and in position which the concentration-depth curves undergo as the result of the more and more prolonged treatment with the "isolated" carbon monoxide is sufficient to show clearly how the rational application of the process of cementation with which we are now dealing permits of obtaining cemented zones in which the principal causes of the phenomena of brittleness and of exfoliation which always manifest themselves to a more or less marked degree in steels cemented

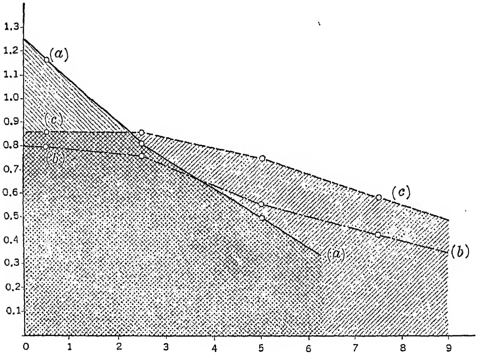

FIG. 151.

by the ordinary processes are eliminated. As a simple reminder of the considerations developed before, I recall here that the principal of these causes are the high concentration of the carbon in the surface zones of the cemented pieces and its rapid decrease as we pass to deeper and deeper layers. Also that this rapid decrease contributes to a very great extent to intensifying the phenomena of liquation of the cementite (or of the corresponding complex carbides of the various special steels) and of the ferrite. These phenomena are the cause, in their turn, of the sudden local variations in the concentration of the carbon which are produced during the cooling of the cemented pieces, to which are due the phenomena of exfoliation of the cemented and hardened zones.

Finally, the possibility of making the form of the cementation curves vary in the manner I have demonstrated indicates the way for successfully cementing also those special steels which by the ordinary processes of cementation furnish excessively brittle cemented zones. The interesting technical results derived from this possibility have already been amply confirmed by practical experience.

It is of marked practical importance that the use of the mixed cement with carbon monoxide as base in the vertical muffle furnaces, permitting (contrary to what occurs when the cementation is carried out with solid cements in the usual boxes) of easily varying the temperature of the cementation and even of interrupting the operation by rapidly discharging and recharging the retorts, furnishes means of raising at pleasure and up to very high limits the *normal* concentration of the carbon in the cemented zones, thus taking advantage of the phenomena which accompany oscillations in the temperature of the cementation. (See p. 160 *et seq.*)

§ 6. SPECIAL CEMENTATION

This section refers to those processes of cementation which, either owing to their purpose or to the special conditions under which they must be put into operation in practice, can not be included in any of the preceding groups.

Leaving aside the processes of electrical cementation, because thus far they have never been applied on an industrial scale, and some others of still less practical importance, there remain the special application to the manufacture of ship armor, and the so-called processes of "metallic cementation," the object of which is to produce the diffusion of elements other than carbon into solid steel.

The chemical laws which are applied in the cementation of armor are the same as those which we have already studied for other cases, so that the rules to be followed are the same. However, the cements which we have called too "sudden" are at a serious disadvantage, for the necessity of extending the cementation to great depths (in general, from 20 to 30 mm.) forces us to protract the operation for a very long time or to carry it out at a very high temperature; and then, in either one case or the other, we know that if cement which is used is not very "mild" the concentration which the ›on attains in the peripheral part of the cemented pieces assumes ⁊ high values, giving rise, especially after the hardening, to dangerous tleness.

Γhis is the reason which has led many manufacturers to abandon rapid more economical cements (such as the well known mixture of carbon and um carbonate) for others considerably slower but "milder," such as ›le wood charcoal or the mixtures of wood charcoal and animal charcoal. ᵌreat advantages are presented, for this special purpose, by the mixed ›nts with carbon monoxide as base, already amply described, and espe- y when use is made of the expedient of "isolating" the action of the car- monoxide in the second phase of the cementation.

ome numerical data will serve to show the variations in the concentration e carbon in the successive layers of the cemented zones which are ordi- y obtained in armor.

Plate of Krupp steel (Cr-Ni) 280 mm. thick, cemented with illuminat- as:

Distance of the analyzed layer from the external surface of the cemented zone (mm.)	Concentration of the carbon, percent.
1	1.75
6	1.50
11	1.03
16	0.88
21	0.66
26	0.42

Plate of chromium-nickel steel of higher nickel content than the ɔ metal. Thickness of the plate, 250 mm. Cementation carried out the mixed cement, the action of the carbon monoxide being isolated end of the operation:

Distance of the analyzed layer from the external surface of the cemented zone (mm.)	Concentration of the carbon, percent.
1	1.02
6	1.04
11	0.97
16	0.92
21	0.72
26	0.64
31	0.57

While the laws which govern the cementation up to such considerable depths are the same as hold for shallower cementations, their practical application must, however, be carried out with special precautions in the case with which we are now dealing, owing to the large masses of the substances which take part in the operation, and require special apparatus and arrangements. These technical details constitute, as a whole, special processes concerning which the manufacturers desire to keep the greatest secrecy, and although I have had occasion to deal with them personally in various establishments, I think it my duty not to publish anything which may have any real practical value. Not wishing, on the other hand, to summarize here the data of no practical value already published by others in various journals, I think it desirable not to develop this purely technical subject at all, but again insist on the fact that, as far as regards the laws which govern the course of the cementation, the considerations which are developed in the first part of this volume hold completely even for these cementations extended to great depths.

We must repeat the same observations as regards the technical applications of "metallic cementation."

We have already referred briefly in the preceding chapters to the results of some scientific investigations on the diffusion of elements other than carbon into solid steel.[1] Later we shall refer also to some patents which claim processes of this kind. I may add here that in the last few years there have been obtained interesting practical results (already protected by patents all over the world) on the diffusion into solid steel of a certain number of elements other than carbon, such as nickel, chromium, manganese, boron, tungsten, etc. Personal reasons prevent me from furnishing here detailed accounts of these results, already successfully applied at the present time on an industrial scale.[1]

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[1] Among others, the works of Boussingault on the diffusion of sulphur (see p. 23); those of Arnold and MacWilliam on the diffusion of various elements (see p. 35); those of Campbell . . . . and several others. The question of the diffusion of sulphur into solid steel has again recently been taken under examination by Grayson (see *The Journ. of the Iron and Steel Institute*, 1910, Vol. I, pp. 287–303). As to the addition of sulphur compounds to the carburizing substances for the purpose of increasing the velocity of penetration of the carbon, it is well to recall the correct observations made by Le Chatelier (see the abstract of the *Revue de Métallurgie*, 1905, p. 120) in connection with a patent of the "Feuerfeste Industrie Gesellschaft" of Dusseldorf, claiming the use of a cement formed of a mixture of carborundum and sodium sulphate. Le Chatelier observes that the fact, proved with certainty, that iron sulphide penetrates with great ease through all the spaces between crystals of ferrite makes it not improbable that the sulphur added to the carburizing mixtures may serve as "vehicle" for the carbon which diffuses into the iron. Account must be taken in practice, however, of the very harmful effects which the presence of sulphur exercises on the qualities of iron.

Considering the phenomena of the diffusion of the various elements into steel from a general point of view, and taking into account, by analogy, the facts observed in the diffusion of carbon, it may be considered that these phenomena must be due either to the intervention of gaseous compounds or to the formation of solid solutions of the elements which diffuse (or of their compounds, such as the carbides) in the iron. The formation of the solid solutions of the metallic carbides in the iron must be considered as the most important factor in the diffusion of the metals into the solid iron in the processes of "metallic cementation" proper.

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[1] In this connection it may be well to point out here how, for some time, industrial practice has showed that several of the elements which Arnold and MacWilliam (see p. 35) had classified among the "fixed" elements (that is, those incapable of diffusing into solid iron) can in reality diffuse into steel in the solid state. Among such elements are manganese and tungsten.

CHAPTER III

THERMAL TREATMENT OF THE CEMENTED PRODUCTS

The cases in which the pieces of cemented steel are used directly, after cementation, without being subjected to further heat treatment, are very rare. It may, in fact, be held that the only such case is where the product, totally cemented, is to be fused in crucibles.

In all the other cases—and they are a very large majority—in which advantage is taken of the difference between the mechanical properties of the carburized zone and those of the nucleus, whose chemical composition has remained practically unchanged, the further operations of hardening, annealing and tempering are the only ones which develop to their full extent the different mechanical properties due to the different degrees of carburization of the steel.

The operations and the apparatus for heat treatment of the cemented products differ in absolutely no respect from the operations which are carried out and the apparatus which are commonly employed in technology for the heat treatment of any other kind of steel.

Thus, for heat treatment of the objects of cemented steel there are used the same heating furnaces (reverberatory, muffle, salt bath, lead bath, etc., heated with coke or gas or electricity) and the same means of cooling (water, salt solutions, oil, air currents, etc.) as are used for the heating and quenching of any object of homogeneous steel.

Apparatus or arrangements for the annealing are the usual ones (hearth or muffle furnaces) and also for the hardening (oil, lead, air baths, etc.). It would therefore be absolutely superfluous to give here detailed information as to the general technology of the heat treatment of the cemented pieces, as those directiors form the subject of a large number of most valuable and complete works.[1] The hardening of steel objects superficially cemented differs from that of objects of homogeneous steel only as to the temperatures at which the quenching and the other heat treatments must be effected. This is owing to the fact that the temperatures at which the various heat treatments of a given steel must be effected depend on the concentration of the carbon in this steel; and therefore the rules for the heat treatment of homogeneous steel of a uniform carbon content can not, evidently, be applied directly to the heat treatments of a cemented piece which has, in its different parts, carbon contents varying between very wide limits.

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[1] See, for example, the volume of Guillet, entitled: *Trempe, recuit, revenu;* that of Grenet: *Trempe, recuit, cémentation et conditions d'emploi des aciers* (Ch. Béranger, Paris, 1911); that of Reiser: *Das Härten des Stahles;* that of Lake: *Composition and Heat Treatment of Steel;* and many others.

It will therefore be well to indicate here how the rules which govern the temperatures adapted to heat treatment of the various types of homogeneous steels may most suitably be applied to the corresponding treatment of the cemented steels, so as to take the best possible advantage of the essential characteristic of the objects manufactured of such steels., *viz.*, the difference in carbon content from the periphery to the nucleus.

A steel object superficially cemented is essentially constituted of two parts, joined to each other by a transition region in which the composition and, therefore, the properties of the metal vary more or less gradually from those of the first to those of the second part. These two parts are the peripheral zone, constituted of a highly carburized steel, and the central part ("heart" or "nucleus"), constituted of a steel whose chemical composition has remained practically identical to that of the original material, while the structure and the mechanical properties have been more or less profoundly altered as the result of the long heating at a high temperature.[1]

It is clear that proper heat treatment of a partially cemented piece can never comprise less than two quenching operations, carried out at two different temperatures, so chosen as to confer the best mechanical properties upon the two constituent parts of the object.

The fundamental problem of the heat treatment of partially cemented pieces consists therefore in choosing the two temperatures in such a way that the useful effects of the two quenchings will be superimposed without harming each other.

Only when the mechanical properties of one of the two parts of the cemented piece have a greatly preponderant importance can it be desirable to limit the heat treatment to that one of the two quenchings which gives the best properties to that part. In such a case, we must be satisfied, as concerns the other part, with the properties which it assumes as the result of the single operation, even though these properties are not the best which a metal of that composition might possibly be given.

In the very large majority of cases we begin by carrying out a first quenching at a temperature sufficient to "regenerate" the steel of the "heart" of the cemented piece, which is always somewhat "burnt," trying to impart to this metal the maximum "tenacity."

This first quenching, called "regeneration quenching," is usually followed by a "hardening quenching," carried out at a temperature lower than the first and designed to impart to the steel of the cemented zone maximum hardness compatible with the brittleness which can be tolerated in the cemented piece.

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[1] It has already been pointed out how some experimenters have held that the increase in the brittleness of the steel of the "heart" of the cemented pieces could be attributed to other causes than to the long heating undergone by it during the cementation, *viz.*, to a modification in the chemical composition of the steel, and especially to an increase in its nitrogen content. It would seem, however, premature to accept such an hypothesis without further and more certain direct proofs.

When the cemented piece is to resist only surface friction, but is not to be subjected to large bending forces nor to shock, the "regeneration quenching" may be omitted; while in cases in which it is not necessary to obtain a very great surface hardness, it is sometimes possible to do without a true hardening proper, merely making an attempt to carry out the single hardening (the "regeneration quenching") at the lowest possible temperature.

But the cases in which this second procedure may be considered advantageous are very rare, owing to the fact that the hardening quenching, always carried out at a relatively low temperature, does not carry with it any marked disadvantage.

On the contrary, the cases in which it is really desirable to follow the first procedure are quite frequent. This consists in the suppression of the regeneration quenching, owing to the fact that this being carried out generally at a high temperature results in marked deformation of the cemented piece. When this procedure is followed, however, it is necessary to carry out the cementation at not too high a temperature (between 850° and 950° C.) so as to avoid producing in the soft steel of the "nucleus" of the pieces such an excess of brittleness as could not be corrected by any tempering, but only by a true regeneration quenching proper.

As a typical example of the cases in which it is often expedient to suppress the regeneration quenching we may mention cups and rings for ball bearings, for which great deformations are more to be feared than the harmful effects of not obtaining maximum tenacity in the soft metal of the nucleus.

To indicate briefly the circumstances which must guide in choosing the heat treatment of partially cemented steel pieces, it is well to consider separately the various cases which present themselves in practice, according to the initial composition of the steel subjected to cementation.

When the cemented objects are made of ordinary carbon soft steel, which, as is well known, suffers more than any other the harmful effects of prolonged heating at a high temperature, the proper choice of the heat treatment has far greater importance than for the majority of other types of special "cementation" steels, for which one of the essential requirements is, usually, that of preserving maximum tenacity in the non-cemented parts.

When studying the heat treatment of a partially cemented piece of steel, we must always assume that the temperature at which the cementation has been carried out has been kept below the lowest limit of the crystallization of the most highly carburized zone of the steel under consideration; for, if this has not been the case, the partial fusion of the mixed crystals will have enormously accelerated the process of carburization at the periphery of the piece, and the formation of a cemented zone of cast iron proper will have rendered the cemented piece absolutely useless. This is the phenomenon which was observed many years back by Mannesmann, and which fixes absolutely the upper limit of temperature, above which partial cementation can not usefully be carried out. No heat treatment would "regenerate" a cemented piece made useless in this way. It is clear that both the metal constituting the "core" and the carburized zone of the cemented piece can not be "burnt" in the true sense of the word, but can only have undergone one of the two typical modifications in structure which manifest themselves when the temperature of heating is somewhat lower than the last transformation point of the steel or is comprised between this temperature and that of the "solidus" for the mixed crystals of the maximum carbon content contained in the steel under consideration.

Now, it is known that both in the one and the other of these two cases the "regeneration" of the steel can be effected by first making it undergo its complete transformation on cooling and then bringing it back for a short time to a temperature a little higher than that of its last transformation point on heating, to quench it, usually, directly from this temperature.

The necessity of making the steel undergo its complete transformation at least once, excludes the possibility of suitably regenerating and hardening the cemented piece without subjecting it to at least a second heating. It is, therefore, not possible to obtain a good product by simply allowing the cemented piece to cool to the temperature suitable for the regeneration hardening and quenching it directly at that temperature.

As to producing the transformation on cooling, it is clear that the simplest way would be to allow the cemented pieces to cool slowly from the temperature of cementation to a temperature markedly lower than that of the last point of transformation on cooling, and, eventually, even to ordinary temperature when the special form of the objects does not give cause for fear of cracking. We have seen, however, that while such a procedure is certainly better than any other in the case of objects of homogeneous steel, it presents in the case of the partially cemented objects the serious disadvantage of liquation of the ferrite and, perhaps, of the cementite during the slow cooling. These disadvantages, which have been discussed in great detail in the first part of this volume, make it preferable to first quench the steel at the temperature of cementation and then heat it very slowly up to the temperature of the regeneration. In this way the steel undergoes, during the part of the slow heating which precedes the first transformation point, a strong recovery which prepares it excellently for the regeneration. Only in the case in which the cementation is carried out at a very high temperature (1050°–1100° C.) is it desirable to let the cemented pieces cool to about 950°–980° before subjecting them to the first quenching. For the reasons already set forth, such a slow cooling can have no harmful effect, for it does not reach the temperature at which the processes of liquation of the ferrite or of the cementite can begin.

As to the temperatures at which the two quenchings—that "of regeneration" and that "of hardening"—must be carried out, these depend on the temperatures of the complete transformation of the two steels constituting the nucleus and the cemented zone. It is known, in fact, that the best results are obtained by carrying out the two quenchings at temperatures slightly above these two respective transformation points.

In an ordinary carbon soft steel, cemented under conditions such that the concentrations of the carbon shall be near 0.9% in the greater part of the carburized zone, the transformation of the soft metal of the "core" is completed at about 900°, while that of the greater part of the metal of the cemented zone is completed a little above 700° C.

Fig. 152, taken from the volume of Grenet already cited, represents the curves of dilatation of the two parts of a cemented carbon soft steel. The position of the points *C* and *G*, which, as is well known, correspond to the end of the transformation during heating, fully confirms the data reported above.

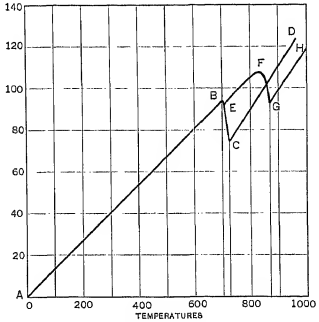

FIG. 152.

Summarizing, then, what has been said in the pages which precede, the heat treatment best suited to an ordinary carbon soft steel, cemented under the usual conditions, is the following:

1. "Regenerating quenching," carried out at a temperature a little higher than 900° C.[1]

This first operation regenerates well the soft part of the cemented piece. Moreover, when in a part of the cemented zone the concentration of the carbon is higher than 0.9%, the heating to a temperature markedly higher than that of the segregation of the primary cementite produces a more or less complete solution of the laminæ of cementite, the permanence of which in the cemented and hardened zones is known to constitute one of the most important causes of brittleness. Moreover, even in the case in which the concentration of the carbon in the cemented zone does not exceed 0.9%, the regeneration quenching acts efficiently as a means of rendering more uniform and gradual the variations in the concentration of the carbon between the various points of the carburized zone, throughout the whole extent of which the steel, at the high temperature at which the quenching is effected, is present in the state of stable mixed crystals.

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[1] It is often advisable to considerably exceed this temperature and to quench from 1000°, since the transformation into γ iron, which destroys the grain, is subject to retardations like all polymorphic transformations. It is on the same principle that Osmond and Cartaud (*Rev. de Mét.*, III, 658, 1896) state that to transform a primitive crystal of α iron into small grains it is necessary to exceed the temperature of the point A_3 "sufficiently and for a sufficiently long time." Industrial practise confirms this theoretical remark. [Note in French Translation—by A. Portevin.]

It sometimes happens, either owing to the special chemical composition of the steel or to the too large dimensions of the object being treated, that the first regeneration quenching does not produce all the effect of which it is capable, either on the properties of the metal constituting the core of the cemented piece or on those of the carburized zone. In these cases it is useful to repeat the quenching a second and sometimes even a third time under the same conditions.

2. "Hardening quenching" carried out at a temperature slightly lower than 800° C.[1]

This second quenching can, in a certain way, be considered also as a regeneration quenching of the steel of the carburized zone, for which the heating at 900° C. (necessary for the "regeneration" of the metal of the core) is too high, in relation to its high carbon content.

The cemented piece must be kept at the temperature necessary for the hardening quenching (about 800° C.) only during the time strictly sufficient to insure that this temperature is thoroughly uniform throughout the whole cemented zone, for too prolonged a heating would produce in the soft metal constituting the core of the piece those characteristic phenomena of crystallization (accompanied by great increase in brittleness) which, as is known, show themselves in all carbon steels heated for a long time at a temperature slightly lower than that at which the transformation on heating ends.

Moreover, if the cemented zone is markedly hyper-eutectic, a prolonged heating at about 800° C. results in agglomerating into masses of considerable dimensions that portion of the small elements of cementite (separated, during the second heating, from the mixed crystals "fixed" by the first "regeneration quenching") which remain after the mixed crystals have become saturated at 800°. As is known, such a process also gives rise to a great increase in the brittleness of the cemented zone and favors the phenomena of exfoliation.

In some cases it may be desirable, for reasons of simplicity and of rapidity, to simplify the complete heat treatment to which I have referred. For cemented carbon steels, these simplified treatments are summarized and concreted by Grenet[1] as follows:

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[1] A fact which seems to have been remarked by no one, and which we have confirmed on steel cemented at 1000° (in a mixture of wood charcoal and barium carbonate), is the increase of brittleness of the core caused by quenching at low temperature after cementation. [Note in French Translation—by A. Portevin.]

Treatment (*a*)—Hardening of the pieces as soon as they are removed from the cementation chambers. This treatment can be usefully applied only to pieces designed to be subjected only to surface friction and not to forces capable of producing fracture or exfoliation.

It is necessary that the pieces should be removed from the cementation chamber (usually, the boxes) while they are still hot (above 800° C.) and quenched immediately.

This process, which has the advantage of being rapid and of imparting great hardness to the surface of the cemented pieces, is not advisable, for it does not permit of effecting the quenching at a well-defined temperature, and regenerates neither the cemented zone nor the core of the pieces.

Treatment (*b*)—After the cementation the piece is allowed to cool, then heated to 950° and quenched in water.

For the reasons which we have already seen, such a treatment acts efficiently in regenerating the soft metal constituting the core of the cemented pieces, imparting to this metal the maximum tenacity of which it is capable, but it certainly is not the one best adapted for the cemented zone, which should be hardened at a much lower temperature.

As to the way of practically conducting the complete thermal treatment, with double quenching, Grenet makes some observations which it may be well to summarize here briefly.

First of all, in the execution of the first "regeneration quenching," which it would be advisable to carry out at 950°, the melting temperature of barium chloride, it is well to remove the piece from the water when its red color is seen to disappear, and this because the rapid cooling of the piece to the temperature of the water (usually below 20° C.) predisposes it to cracking and exfoliation during the succeeding heating for the "hardening quenching." On the other hand, the hardening, even when interrupted in the manner indicated above, is no less efficacious in the regeneration of the soft metal of the core than is the complete quenching, for when the red color of the piece totally disappears the temperature has certainly fallen below 600° C., that is, much below the temperature at which the transformation on cooling is totally effected. Moreover, the efficacy of the interruption of the process of rapid cooling in the water, in diminishing the probability of the formation of cracks during the succeeding heating, is evident even if this interruption takes place at a temperature little higher than 200° C. It is therefore clear that no special skill is necessary to have the interruption of the hardening, executed as above described, give all the useful effects of which it is capable.

Effects analogous to those of the interruption of the hardening can be obtained by the various well-known modifications of the quenching adapted to "deadening" its effects; as, for example, by quenching the piece in oil or in hot water.

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[1] *Trempe, recuit, cémentation et conditions d'emploi des aciers* (Béranger, Paris, 1911).

The necessity of regenerating the metal of the core of cemented objects makes it very harmful to apply the partial quenching, which is often successfully used on homogeneous steel, when it is desired to harden only a part of it. It is clear, in fact, that if the hardening is limited to a part of the cemented object, the metal constituting the other part, always considerably altered by the long heating which accompanies the cementation, will remain brittle.

The partial hardening can be applied in the second part of the complete, double quenching, thermal treatment. In this case, in fact, the metal is already completely regenerated by the regeneration quenching effected on the whole mass of the cemented object, and the heating at 800° C. which precedes the hardening quenching, being conducted rapidly, does not produce practically appreciable alterations, not even in the part of the metal which does not undergo the second hardening. This last observation holds for those parts of the metal which it is desired to keep soft (and therefore not to immerse in the hardening bath) which could not have been protected from the second heating owing to their closeness to the parts to which it is desired to impart the maximum hardness.

When the simplified thermal treatment which we have called "*treatment* (*b*)" (simple quenching at 950°) is applied, Grenet advises to heat the whole of the cemented piece to the quenching temperature, then immersing in the hardening bath only the part which is to be hardened. Grenet advises, in this case, to immerse the whole piece in the water and to remove the part which is not to be hardened as soon as the red color is seen to disappear.

Experience with this last procedure, constituting, as is clear, a special application of the so-called "recovery by heat proper," has showed me that in the majority of cases great practice is necessary to obtain constant results with precision.

The difficulty in the practical application of the processes of partial quenching to cemented pieces puts still more clearly in evidence the practical importance of the methods for the "local protection" of the pieces subjected to cementation.

To show what may be the effects of the prolonged heating which accompanies the cementation, and the efficacy of the regeneration quenching on cemented ordinary carbon soft steels, we will cite some numerical data from the article by Guillet in the *Génie Civil*, already frequently referred to.

The following table shows well the increase in the brittleness of an extra-soft carbon steel as the result of the prolonged heating. In all seven of the experiments to which the numbers of the table refer, the heating was conducted by keeping the temperature constant for eight hours. The resistance to shock was determined on a Fremont test piece 8 × 10 mm.

From the data reported, it follows clearly that the increase in brittleness of the steel examined, due to rise in temperature of the heating, becomes a maximum for just the interval of temperature (850°–1000° C.) within which the increase in the velocity of the cementation due to a given increase in the temperature is a maximum.

Temperature at which the heating was effected	Resistance to shock (kilogram-meters)	Temperature at which the heating was effected	Resistance to shock (kilogram-meters)
800° C.	26	1000° C.	4
850° C.	28	1050° C.	3
900° C.	15	1100° C.	4
950° C.	12		

The increase in the brittleness of a carbon soft steel due to increase in the temperature of the heating, however, manifests itself to a degree varying within wide limits for even small variations in the composition of the steel. It would certainly be most useful to have precise data on the relations which connect the two variables.

From a series of experiments carried out by Guillet, it seems to be proved that the effects produced by cementation (carried out with cements having carbon monoxide as base and free from cyanides) on the mechanical properties of the soft metal constituting the core of the cemented pieces are identical to those produced by heating in a neutral medium, at the same temperature and for the same time. These effects would therefore be due exclusively to the action of the heat treatment which accompanies the cementation.

Other experiments carried out by Guillet with nitrogenous cements gave extremely irregular results, from which it is difficult to draw conclusions as to an eventual chemical action exercised by the cement on the metal of the core of the cemented pieces.

As an example of the effects which the regeneration quenching may exercise on the properties of the soft carbon steel constituting the core of the cemented pieces, I report in the following table some results of shock tests, also taken from the memoir of Guillet, cited above.

No. of the extra-soft steel used	Original bar heated at 925° C. and allowed to cool in the air (kilogram-meters)	Original bar quenched at 925° C. in water at 20° C. (kilogram-meters)	Bar cemented for 4 hours at 1000° C., not quenched (kilogram-meters)	Bar cemented for 4 hours at 1000° C. and quenched at 1025° C. in water at 20° C. (kilogram-meters)
1st type......	28	32	10	30
2nd type......	32	32	12	28
3rd type......	28	34	9	3
4th type......	33.4	34.5	31	33

The shock tests were made on test pieces of the Mesnager type, obtained *wholly* from the core of the bars. The last is a condition absolutely essential if the results of the shock tests are to represent the true brittleness of the metal constituting the core of the cemented pieces.

The numbers contained in the table reproduced above, while showing, in general, the regeneration quenching to be an efficient means of diminishing the brittleness of a carbon soft steel heated for a long time to a high temperature, also show that the extent of the effects which can be obtained by such a heat treatment may vary between very wide limits with variation in the composition of the steel used.

As a summary example of the specific effects of the various quenchings on the mechanical properties of the two parts of a piece made of an ordinary cemented extra soft steel, we have the following table, also taken from the memoir of Guillet which has been already cited several times:

Treatments	Resistance of core to shock in kg.-m. (Mesnager test piece)	Surface hardness determined by Shore method		
		Mean	Minimum	Maximum
Non-cemented steel, heated at 925° C. and cooled in air.	20.6	....	....	....
Non-cemented steel, quenched at 925° C. in water.	23.8	....	....	....
Steel cemented at 1000° C. for 1.2 mm. and cooled slowly.	13.5	38.50	38	40
Steel cemented at 1000° C. for 1.2 mm. and quenched at 1000° in water.	23.2	79.80	78	83
Steel cemented at 1000° C. for 1.2 mm. and quenched twice in water, at 1000° C. and at 750° C.	25.5	84.0	81	88

The most easily recognizable effect of the regeneration quenching on the core of the cemented pieces is the change in the appearance of the surface of fracture. This surface, which before the quenching has a "granular" appearance, assumes a "fibrous structure" as the effect of the quenching.

The effects produced by a given series of heat treatments on the mechanical properties of an ordinary carbon soft steel vary between very wide limits with variation in the composition of the steel subjected to the treatment. The experimental data at present known do not permit of expressing in numbers the relations between these variations. As a general rule it may be held that for a cemented soft steel the brittleness produced by the prolonged heating is the greater, and the efficacy of the quenching the smaller, the higher the initial concentration of the carbon. Save for few exceptions (as, for example, the manufacture of matrices, etc.), an ordinary carbon soft steel designed for the manufacture of cemented mechanical pieces must not contain more than 0.2 percent of carbon. This limit can be exceeded only for some special steels; for example, the nickel steels.

A too high content of manganese (0.5–0.7 %) or of silicon (more than

0.3 %) also increases the brittleness produced by the prolonged heating during cementation, and diminishes the efficacy of the regeneration quenching.

All the data just reported hold for the case where the steel used for cementation is an ordinary soft carbon steel.

The use of some well-defined types of special steels permits of simplifying the thermal treatment which is to follow the cementation, of greatly increasing its efficacy and of rendering its results considerably more certain.

The special steels most frequently used for cementation are the soft nickel steels. The superiority of the soft nickel steels over the ordinary carbon steel, for this purpose, is due to the fact that the increased brittleness produced by a definite heating at a high temperature is considerably less for the steels of the first type than for those of the second. This fact is seen most clearly from the numbers contained in the following table, also taken from the memoir of Guillet which has been already several times cited.

Although Guillet does not indicate the temperature at which the heating was carried out and these data can, therefore, be considered only as to their relative value, they show very clearly the fact set forth above. This is confirmed by the observation, many times repeated by a large number of experimenters, that, if the length and the temperature of heating are equal, the pearlite remains considerably finer, more uniformly distributed, and much more subdivided, in a nickel steel than in a carbon steel.

Length of heating	Resistance to shock	
	Ordinary extra-soft steel	Extra-soft steel with 2 % of nickel
Normal heating	20 kilogram-meters	60 kilogram-meters (not broken)
Four hours	4.5 kilogram-meters	60 kilogram-meters (not broken)
Six hours	4.0 kilogram-meters	60 kilogram-meters (not broken)

Besides this, we have seen that, with the same heat treatment, in partially cemented nickel steels, those phenomena of the liquation of the cementite and of the ferrite which constitute the principal cause of the exfoliation of the cemented and hardened pieces make themselves felt to a considerably less degree than in ordinary carbon steels.

It is indeed true that together with these marked advantages the nickel cementation steels present some disadvantages, but these disadvantages, which can for the most part also be eliminated by proper conduct of the cementation, are not of great practical importance and are almost always largely compensated by the advantages already referred to.

One of the disadvantages most frequently attributed to the nickel cementation steels is the greater slowness with which the cementation proceeds in them. Now, while this fact may manifest itself with the use of certain cements it is, however, quite certain, as was shown clearly in the first part of this volume, that this does not manifest itself when the mixed cements with carbon monoxide as base are used; with these the cementation of the nickel steels is effected with the same rapidity as that of the ordinary soft carbon steels.

Greater practical importance must be attached to the other disadvantage, brought out by many investigators, of the lesser hardness which, with the same treatment, is possessed by the carburized zones in nickel steels as compared with the carburized zones of ordinary carbon steels under identical conditions. This fact is due not only to the different effects produced by a different quenching on the steels of the two types, but also to the smaller concentration which (especially for steels containing more than 3% of nickel) the carbon attains in some cases in the cemented zones of the nickel steels as compared with that in the ordinary soft carbon steels cemented under identical conditions.[1] It is easy, however, to eliminate this disadvantage with certainty by making use of one of the numerous means described in the first part of this volume for raising the concentration of the carbon in the cemented zones.

As to the various other disadvantages attributed to the use of soft nickel steels as cementation steels, such as the tendency to the formation of flaws difficult to eliminate, the great heterogeneity, etc., they may to-day be considered as totally eliminated, thanks to the great perfection attained in the manufacture and in the preliminary treatment of the special steels of every kind.

We will now consider the heat treatments most suitable for developing the useful properties characteristic of the nickel steels when used for cementation.

To treat of this subject with sufficient clearness, it is necessary to subdivide the soft nickel steels used for cementation into two groups; the first of these includes the steels containing less than 4% of nickel, while in the second the nickel content exceeds that value and may, in practice, rise as high as 6–7%. We will assume the heat treatment of homogeneous nickel steels as being known and will give only the special rules which hold for the thermal treatment of these steels after having been cemented.

1. Among the cementation nickel steels belonging to the first group, the one most frequently used is that with 2% of nickel. This steel cements in almost exactly the same way as the carbon steel, and furnishes cemented zones capable of assuming great hardness on quenching in water.

The fact that the brittleness of the core of the cemented pieces manufactured of this steel does not increase much as the result of the heat treatment which accompanies the cementation, together with the fact that the temperature of transformation, during heating, of the metal constituting this core is considerably lower than that of soft carbon steels, makes it possible to produce regeneration of the core perfectly well, in the case with which we are dealing, by quenching at 850° C., in water or in oil. But since the cemented zone of the steel with 2% of nickel can be hardened at a temperature markedly higher than the normal quenching temperature of a carbon steel of equal carbon content, it follows that the regeneration hardening carried out under the conditions just indicated is amply sufficient, in the majority of cases, as a hardening quenching also.

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[1] See p. 140.

It is seen, therefore, that in case the cemented and hardened piece is not to be subjected to exceptional stress, the heat treatment of the cemented pieces is markedly simplified by the use of the soft steel with 2% of nickel.

But, even for the steel with 2% of nickel, the single quenching carried out under the conditions as indicated is only a simplified treatment, whose practical usefulness consists especially in shortening the operations and in diminishing the causes of deformation of the pieces. Even for these steels considerably better results are obtained by separating the two quenchings of "regeneration" and of "hardening," and by effecting each one of them at the most suitable temperature, fixed by the transformation points of the metal of the core and of that of the carburized zone.

It is well known that the point of transformation on heating and that on cooling, points which for carbon steels are quite close to each other, are farther removed from each other in nickel steels the higher the nickel content. This fact, together with the smaller velocity with which the variations in the concentration between the various points in the solid solutions[1] are effected in the nickel steels, leads to raising somewhat the temperature of the regeneration quenching.

The complete thermal treatment of a cemented piece of soft steel with 2% of nickel is therefore as follows:

(*a*) Quenching in water, from 960°–980° C. The piece is removed from the water when it ceases to be red.

(*b*) Quenching in water from about 740°–770° C.

To show the efficacy of this heat treatment, the numerical data in the accompanying tables, also taken from the memoir of Guillet previously cited, are of value.

The data in Table *A* show the efficacy of the regeneration quenching effected at about 1000° C. (cases 4 and 5).

The data in Table *B*, next, show the advantage of carrying out the hardening quenching at a lower temperature (about 750° C.).

The cemented steels containing a proportion of nickel somewhat higher, but not more than 3.70–4%, are treated in an entirely analogous way.

2. Soft nickel steels of the second group, containing about 6–7% of

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[1] Of this fact we have already seen a proof in the lesser extent of the phenomena of liquation.

nickel, are characterized by the fact that after the cementation the point of transformation of the metal on cooling, constituting the carburized zone, is lowered almost to the ordinary temperature. We have described, in the first part of this volume, the interesting observations made by Guillet on the phenomena which take place in the cementation of these steels.

TABLE *A*

No.	Treatment	Resistance to shock (kilogram-meters)
1	Steel with 2% of Ni and 0.1% of C heated at 925° C., allowed to cool in the air	33.4
2	The same steel, quenched in water at 925° C.	34.5
3	The same: cemented at 1000° C. for 1.2 mm. and slowly cooled	31.0
4	The same: cemented in an identical manner and quenched in water at 1000° C.	33.5
5	The same: cemented in an identical manner and quenched twice in water at 1000° C. and at 750° C.	36.0
6	The same: cemented in an identical manner and quenched in water at 750° C.	32.0

TABLE *B*

No.	Treatment	Hardness numbers		
		Mean	Minimum	Maximum
1	Cemented pieces, not quenched	39.37	39	40
2	Cemented pieces, quenched at 1000° C.	78.05	69	84
3	Cemented pieces, quenched at 750° C.	86.56	85	88

For the same reasons already indicated in connection with the steels of the preceding group, and especially on account of the greater slowness with which the concentration equilibrium of the mixed crystals establishes itself, it is necessary, in order to obtain a really efficient regeneration of the metal of the core, to carry out the regeneration quenching at a temperature markedly higher than that which would be defined by the end of the transformation on heating. The most suitable temperature for the regeneration quenching of a cemented steel with 6% of nickel is, according to Guillet, 850° C., while for the hardening quenching Guillet indicates 675° C. as the most suitable temperature.

In the following table, also taken from Guillet, are collected some results of hardness determinations with the Shore apparatus on steel with 6% of nickel, cemented and quenched in various ways:

No.	Treatment	Hardness numbers		
		Mean	Minimum	Maximum
1	Cemented pieces, not quenched	35.6	34	38
2	Cemented pieces, quenched at 700° C.	68.7	60	80
3	Cemented pieces, heated at 750° C. and quenched at 650° C.	62.7	60	70

As is seen, the results oscillate between quite wide limits, but for these high nickel steels the hardness of the cemented and quenched zone does not reach as high values as for ordinary steels. This last fact is probably due to their tendency, already noted, to retain considerable proportions of γ-iron, as well as to the effect of not very energetic quenching. When it is not necessary to impart very high tenacity to the metal of the core, and great hardness in the cemented zone is not to be obtained, the cemented objects made of soft steel with 7% nickel can simply be allowed to cool slowly after the cementation, as practised by Guillet and described already in the first part of this volume. The principal advantage which this presents consists in its great simplicity, and in the fact that it permits of avoiding the deformations which always accompany the quenching of any steel object.

The following table contains the results of some hardness determinations made by Guillet (with the Shore apparatus) on a steel containing 7% nickel and 0.12% of carbon, cemented to a depth of 1 mm. and not hardened by quenching.

The determinations were repeated after having removed successively three layers of the cemented zone, each 0.2 mm. thick; there was thus obtained an approximate indication of the variations in the hardness of the various successive layers of the cemented zone:

No.	Treatment		Hardness numbers (Shore)		
			Mean	Minimum	Maximum
1	Piece cemented to 1 mm., not quenched		18.5	17	21
2	Piece cemented to 1 mm., not quenched, from which is removed a layer having a thickness of —	0.2 mm.	26.5	26	27
3		0.4 mm.	24.5	24	25
4		0.6 mm.	20.2	20	21

The treatment just indicated presents some disadvantages, however. The first of these consists in the small hardness imparted to the cemented zone; this is seen clearly in the last table. The second disadvantage lies in the fact that the core of the cemented pieces is not regenerated.

This disadvantage can be avoided in part by subjecting the cemented pieces to a second heating followed by a cooling in the air; in this case, however, the process loses its simplicity, although retaining the value of avoiding the deformation of the pieces.

The last disadvantage of the method with which we are dealing is the necessity of using steels of very high cost.

When it is necessary to obtain cemented zones capable of assuming great hardness without excessively-energetic quenching, it is quite well to use cemented soft steels containing small quantities of chromium, varying, in general, from 0.6%. to 1.3 %. The presence of such quantities of chromium does not markedly modify the thermal transformations of the steel, so that the heat treatment of cemented pieces made of chromium soft steels can be carried out by applying the rules for ordinary carbon steels.

It is well, however, to remember that the presence of the chromium tends to render more appreciable the harmful effects of the prolonged heating on the metal in the core of the cemented pieces; this renders the regeneration quenching indispensable for cemented pieces of chromium soft steel.

In the table following (Guillet) are collected some data obtained by the various heat treatments of soft chromium steels.

The property of these steels of assuming great hardness in the cemented parts as the result of even relatively mild quenching renders them very useful for the manufacture of pieces which, after cementation, are to be subjected only to quenching in oil or in boiling salt water, so as to avoid deformations as much as possible.

No.	Heat treatment	Composition of the steel	
		Cr = 0.70 % C = 0.05 %	Cr = 1.20 % C = 0.05 %
1	Resistance of annealed metal to shock.............	32 kg.	25 kg.
2	Resistance of quenched metal......................	22 kg.	15 kg.
3	Resistance of metal heated four hours at 1000° C....	6 kg.	5 kg.
4	Resistance of metal after double quenching..........	26 kg.	20 kg.

The chromium-nickel soft steels are at present used on a very large scale as cementation steels for similar purposes. The thermal treatment of cemented pieces made of these steels does not differ appreciably from that described for the nickel steels of equal nickel content.

The presence of nickel (usually in proportions varying from 2 to 3%) together with the chromium renders less marked the increase in brittleness of the core due to the heating which accompanies the cementation, while it no longer appreciably diminishes the hardness which a definite quenching can impart to the cemented zone.

The consequence of the first fact is that it is possible to use without disadvantage chromium-nickel steels for cementation having an initial carbon content up to 0.3%, which is higher than the maximum allowed in the other steels used. The second fact renders these steels, for the reasons to which I referred in speaking of the chromium steels, especially adapted to the manufacture of pieces subjected to strong shocks and which must not be appreciably deformed as the result of the quenching; such, for example, are certain gear-wheels.

We have also seen (see p. 334) that these steels cement more rapidly and better than carbon steels.

There are sometimes used cementation steels containing (usually together with chromium and nickel) small quantities of tungsten, molybdenum, and vanadium. The heat treatment of these steels does not differ markedly from that for steels containing equal amounts of the other elements (C, Cr, Ni).

Moreover, it has not yet been proved with certainty that the advantages conferred by these elements upon the characteristic properties of a cemented steel justify their high cost.

For the process of tempering (rarely applied to cemented steel objects) and of annealing, the same rules hold for cemented steels as are followed for homogeneous steels.

We have already seen, in the first part of this volume and in Chapter II of the second, what useful practical results can be obtained by subjecting the cemented steel objects to a heating, carried out under definite conditions, adapted to facilitating the processes of "equalization" of the concentration of the carbon between the successive layers of the cemented zone. These processes are to be considered rather as true chemical processes, due to the intervention of carbon monoxide, than as simple heat treatments.

There remains to be considered briefly a phenomenon which almost constantly accompanies the hardening of every kind of steel pieces, but which in the case of the quenching of cemented pieces assumes special importance, *viz.*, the phenomenon of the deformation of the pieces.

The simple cementation itself causes deformation of the pieces, especially if it is carried out at a high temperature and if the pieces are charged into the cementation chamber without being well supported at every point, by the cement or by the other pieces or by special supports. These deformations are very easily accentuated in the successive quenchings. This fact and also the fact that the changes in volume which hardening produces in the metal of the core and in that of the cemented zone are not identical especially predispose the cemented pieces to deformation on hardening.

For these reasons, and also owing to the ease with which the cemented and hardened zones break on attempting to straighten out the deformed pieces, the hardening operation is particularly delicate and difficult.

The deformations during cementation are especially marked in pieces

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[1] However, practise has shown that following the hardening quenching by a light tempering diminishes the brittleness of the teeth of gear wheels cemented by a mixture of wood charcoal and barium carbonate. The tempering diminishes the internal strains produced by quenching in the cemented layer where the carbon content varies rapidly. [Note in French Translation—by A. Portevin.]

which have previously undergone extended mechanical treatment (drawing, rolling, forging, etc.). For such it is well to have a heating and a straightening out operation precede the cementation; this is much easier when done on pieces which have not been cemented.

When the cemented pieces are to be subjected to double quenching, it is very desirable to straighten them out accurately and almost completely after the first quenching (*regeneration*) when, as we have seen, they are not brittle. Moreover, at this point of the treatment even a considerable softening of the metal does not harm the final result of the complete thermal treatment, so that, especially in the cases in which the deformations are very strong, the pieces which are to be straightened out can be heated even up to dark redness. Then the pieces, almost perfectly straightened, have to undergo only the second quenching (*hardening*), which deforms them but slightly. In this way, the completely hardened, and therefore more brittle, pieces have then to submit to only small stresses to be completely straightened.

This last straightening must be carried out with considerably more care than is necessary in the case in which hardened pieces of homogenous steel are to be straightened out. During this operation it is sometimes expedient to heat the pieces to about 80°–100° C. to diminish their brittleness.

The procedures and the apparatus which are used for straightening the cemented and hardened pieces do not differ in any respect from those which are used in all the other ordinary cases.

It is well to remember, however, that in the straightening of cemented and hardened pieces, especially if done cold and after the "hardening quenching," it is necessary, as far as possible, to avoid using forces which tend to elongate the cemented zone, as the metal which constitutes the latter can undergo practically no elongation after the hardening, and therefore breaks away with the greatest ease under such forces. To avoid this, it may sometimes be necessary (as happens, for example, in the case of cemented armor plate) to deform the piece artificially before the hardening, so as to be sure that after the hardening there shall remain a deformation in exactly the desired direction, so that the straightening, when cold, can be carried out without subjecting the cemented zone to *tensile* stresses.

CHAPTER IV

METHODS FOR CONTROL OF CEMENTATION

The technical methods used for proper conduct of cementation do not, in general, differ essentially from those which are used for the control of the majority of the other processes in the metallurgy of iron.

In this chapter I propose to briefly pass in review some of these methods, stopping only to indicate some details in those cases where the application of a definite method to the control of the processes of cementation or of their products must be made according to special circumstances.

In the technology of cementation it is necessary, first of all, to exercise rigorous control over the raw materials; and then it is necessary to control with precision the temperatures at which the various processes are effected. Excepting in special cases, it is also necessary to follow the course of the carburization during the cementation and then to control it in the finished product. Finally, it is also necessary to make sure that the cemented product has really acquired the required properties after it has undergone the various treatments to which it is subjected after cementation.

§ 1. CONTROL OF THE RAW MATERIALS

The general methods for chemical and mechanical control of cementation steels naturally differ in no way from those followed in general for the control of steels intended for varied uses. Therefore, on these methods it is desirable to dwell only briefly.

There are, however, two points in the control of the steels used as raw materials for the manufacture of machine parts cemented superficially which assume considerable importance. First of all, it is absolutely essential for the success of the cementation that the steel used should be throughout its whole mass as homogeneous as possible.

It is easy to understand how this condition is considerably more important in a steel which is to be cemented and used directly after the cementation, without undergoing a further fusion, than in any other case. In fact, in a steel which is to be used directly as furnished by fusion, the heterogeneities in composition remain such as they were in the crude piece, but in a steel which, before being machined, has undergone heat mechanical treatments (forging, rolling, etc.) or thermal treatments (quenching, annealing, tempering, etc.) the heterogeneities in composition are generally diminished, and at any rate they are certainly not increased. On the other hand the effects of the cementation (and especially the depth of the cemented zone, the concentration of the carbon contained in it, etc.) vary to a very marked extent with variations in the original composition of the steel subjected to the cementation, so that, to the heterogeneities pre-existing in the steel, are added those which are caused by the different way in which the cementation proceeds in the parts where the composition of the steel is different. A second fact is the presence of veins of slag in the mass of the steel which may give most defective cemented pieces from steel of good mechanical properties.

It is well known, in fact, that small quantities of slag contained in the body of a rolled or forged steel may not exercise a deleterious effect on the various mechanical properties of this steel, and especially on the resistance to tension and to bending when the tension or bending test pieces are taken "longitudinally" or with their major axis parallel to the direction of the lamination. When, however, this same steel is subjected to cementation, the smallest grains of slag become (as we have already seen) centers of "blisters" more or less large according to the nature of the slag and to the conditions under which the cementation was carried out, but always such as to harm the good mechanical properties of the steel to an extent enormously greater than the effect of the original slag on the original steel.

We therefore see clearly the special importance of the examination of the homogeneity of the metal used, and of the greater or lesser proportion of slag contained in it.

Valuable information on this head is afforded by the macroscopic and microscopic investigation of sections of the steel, polished and etched with suitable reagents.

We must assume these tests to be well known, and it is superfluous to enter here into details.

We will add here, as a simple concrete example, some numerical data which will serve as an approximate indication of the limits within which, in general, it is desirable to keep the data of the chemical and mechanical control. Following are some of the conditions established by Guillet for the standard specifications of the "De Dion-Bouton" works, which, as is known, are among the few automobile factories which have organized a serious control of their materials. I take the following data from the interesting memoir published last year by Guillet in the *Gênie Civil.*[1]

1. *Ordinary Rolled Cementation Steel.*—Chemical characteristics:

Manganese	not over	0.40 percent.
Sulphur	not over	0.04 percent.
Phosphorus	not over	0.05 percent.
Carbon	from	0.05 to 0.10 percent.

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[1] *Le Génie Civil,* 1911, Vol. LIX, Nos. 8–14.

Mechanical characteristics:

(*a*) On metal annealed at 900° C.

Tensile strength	= 37 kg. per sq. mm. (±3)[1] (53,000 lb./sq. in. ±4,000)
Elongation, not less than	30 percent. (−2)
Contraction of area, not less than	70 percent. (−5 when *T.S.* > 38)
Tensile strength + elongation, not less than.	67 (kg. + percent.)
Hardness (Brinell)	= 110 (±10)

(*b*) On metal hardened in air at 900°–925° C.:

Resistance to shock (ρ):

Longitudinally, on small Charpy test piece	18 or over
id., Mesnager test piece	25 or over
Transversely, on small Charpy test piece	13 or over
id., Mesnager test piece	20 or over

2. *Nickel Cementation Steel.*—Chemical characteristics:

Nickel, not less than	2.0 percent. (−0.2)
Manganese, not over	0.40 percent.
Sulphur, not over	0.04 percent.
Phosphorus, not over	0.05 percent.

Mechanical characteristics:

(*a*) On metal annealed at 850° C.:

Tensile strength	= 41 kg./sq. mm. (±3) (58,500 lb./sq. in. ±4000)
Elongation, over	28 percent. (−2)
Contraction of area, not less than	70 percent. (−5)
Tensile strength + elongation, not less than	69 (kg. + per cent.)
Hardness (Brinell)	= 120 (±10)

(*b*) On metal hardened in air from 900°–925° C.:

Resistance to shock (ρ):

Longitudinally, on small Charpy test piece	20 or over
id., Mesnager test piece	30 or over
Transversely, on small Charpy test piece	15 or over
id., Mesnager test piece	25 or over

(*c*) On metal quenched in water at 900° C.:

Tensile strength, under	70 kg. sq. mm. (100,000 lb./sq. in.)
Elongation, over	15 per cent.

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[1] The values in parentheses indicate the tolerances allowed.

3. *Chromium-nickel Cementation Steel (First Class).*—Chemical characteristics:

Nickel = 2.5 percent. (±0.5)
Chromium = 0.60 percent. (±0.3)
Manganese = 0.40 percent. or less
Sulphur = 0.04 percent. or less
Phosphorus = 0.05 percent. or less

Mechanical characteristics:
(*a*) Metal annealed at 850° C.:

Tensile strength = 65 kg. (±5) (93,000 lb./sq. in. ± 7,000)
Elongation = 20 percent. (−2) or over
Contraction of area = 55 percent. (−3) or over
Tensile strength+elongation = 85 (kg.+percent.) or over
Hardness (Brinell) = 170 (± 20)

(*b*) Metal hardened in oil at 850 ° C. and annealed at 600° C.:

Tensile strength = 80 kg./sq. mm. (±5) (114,000 lb./ sq. in., ±7,000)
Elongation 14 percent. (−2) or over
Contraction of area 35 percent. (−3) or over
Tensile strength+elongation 94 (kg.+percent.) or over
Hardness (Brinnell) = 225 (±25)

Resistance to shock (ρ):

Longitudinally, on small Charpy test piece	12 . or over
id., Mesnager test piece	15 . or over
Transversely, on small Charpy test piece	8 . or over
id., Mesnager test piece	10 . or over

Besides these, which represent the types usually employed, others of different compositions find quite wide application at present.

The semi-hard steels with 0.3% to 0.4% (and sometimes up to 0.55) of carbon are used as cementation steels in some special cases (for example, for punches, moulds, frogs, etc.); the steels of high nickel content, brought into practise by Guillet (see p. 52); the vanadium steels, which are said to be largely used to-day by the American automobile factories;[1] the chromium-nickel steels for armor; and still many others. Naturally, I can not stop to describe here the conditions of control of these various types of cementation special steels. The chemical and mechanical conditions which they must satisfy vary within very wide limits. It may, in fact, be held that all these conditions must be studied separately, in turn, whenever it is desired to obtain definite special results. In all the other ordinary cases it is preferable to use types of steels analogous to those whose characteristics are given above, since precise and well-defined rules can be applied for their cementation.

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[1] On the real value and on the mechanical properties of the vanadium cementation steels, there have thus far been published no data which are complete or precise. For simple information I report the data in the following table, taken from a Note of Schindler (see *Journ. of the Iron and Steel Institute*, 1908, I, p. 179) on the use of chromium-vanadium steels in cemented machine pieces. The numbers refer to pieces cemented to a depth of

A test of exclusively *preliminary* character, to which it is customary in practice to subject every cementation steel, consists in annealing a specimen, cutting it and breaking it. If the surface of fracture thus obtained has not a fibrous appearance, it is quite difficult for the steel examined to possess one of the properties essential for its acceptance—the faculty of being "regenerated" as the result of hardening. The very great technical importance of this property is evident.

§ 2. CONTROL OF THE TEMPERATURES OF CEMENTATION AND QUENCHING

We have already seen that the temperature at which the cementation is effected influences very intensely the velocity of the cementation, the maximum concentration reached by the carbon in the cemented zone, and also the "distribution" of the carbon in this zone. This may cause two cementations, carried out at two temperatures differing from each other only by a few degrees, to furnish products possessing profoundly different characteristics. The necessity of knowing with precision and of being able to regulate with the greatest certainty the temperature at which the cementation is effected is therefore evident. The necessity of being able to know exactly at any moment the temperature at which the cementation is carried out makes itself especially felt when this cementation is conducted at a temperature varying more or less rapidly between definite limits, instead of at a constant tempera-

one-twentieth of an inch. The mechanical tests—only statical—were made on the metal of the "heart" of the pieces, after having removed the cemented zones on the wheel.

	Common carbon soft steel	Chromium-vanadium steel
Limit of elasticity (tons per sq. in.)........	20.42	34.13
Breaking load (tons per sq. in.)...........	32.36	45.75
Elongation (on 2 in.)....................	34.5%	22.0%
Contraction............................	54.2%	61.6%

In the note cited above, neither the composition of the two steels nor the heat treatment to which they were subjected after the cementation are indicated precisely.

The author holds that his chromium-vanadium steel is especially adapted to making cemented machine parts designed to bear very variable forces.

ture, as is usually done. This, for example, is done (as we have seen on pp. 159-166) when advantage is taken of the oscillations in the temperature of the cementation to raise the concentration of the carbon in the cemented zones. We have seen that this procedure is followed especially when using "mixed" cements, and we shall see shortly that precisely with these cements a frequent measurement of the temperature is easiest.

The pyrometers which are used for the measurement of the temperature of cementation do not differ from those which are used for the control of the other metallurgical processes, except that the special conditions in the majority of the cementation processes render the use of some types of pyrometers by far preferable to other types which otherwise might appear more advantageous. Moreover, the pyrometric measurements in the cementation apparatus will not have a precise significance and will not furnish useful data unless carried out under certain definite conditions, depending on the cement used and on the way of conducting the operation. In fact, we have seen that the greater part of the solid cements used in industry are very bad conductors of heat, so that quite a long time is always necessary for complete temperature equilibrium to be reached throughout the mass in the cementation boxes;[1] therefore the measurement of the external temperature of the cementation boxes, even if carried out at frequent intervals during the heating, cannot furnish precise data as to the *true* temperature of the cementation, or the temperature of the region of contact between the surface of the steel objects and the cement. To get that, we must know the law of propagation of heat in the mass which fills the boxes. But it is evident that the velocity of the propagation of heat from one point to another of the mass under consideration is maximum when the two points form part of a same piece of steel, minimum when between the two points is interposed the cement only, while, when between the two points considered are interposed alternating masses of steel and of cement, this velocity has an intermediate value between these two extremes and is greater the greater the proportion of the steel as compared with that of the cement.

It is therefore evident that the propagation of heat in a charged box will in general be irregular and will depend, even more than on the thermal conductivity of the cement, on the quantity, the form and the position of the steel pieces contained in it. So that, to deduce with precision from the measurements (even if repeated frequently) of the external temperature of the boxes the temperature reached at various times in the different regions of the charge, the measurement of the thermal conductivity of the cement alone will certainly not suffice.

A sufficiently precise deduction of this kind can be made only in case the same pieces of steel are always to be cemented, and under identical conditions. In this case alone is it possible to make once for all a direct experimental determination of the velocity of propagation of heat in the mass constituting the charge of the boxes and then regulate, on the basis of the results thus obtained, the length of the successive cementations carried out under identical conditions, either as regards the method of making the charge, the raw materials used, the operation of the furnace, or, finally, the dimensions and the form of the boxes used. In any other case it would be illusory to consider that a procedure of the kind just indicated can furnish data of any exactness on the propagation of the heat in the mass constituting the charge of the boxes, and only when it is not necessary to obtain perfectly definite results can this procedure be used, even though complete identity between the conditions under which the operation is effected and those under which the test was carried out is not realized.

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[1] See, for example, the data reported on pp. 314-315.

When the conditions which I have indicated above are not realized, it is not possible to obtain with certainty and precision pre-established results from cementations carried out in the usual cementation boxes charged cold, except by working in such a way as to be able to determine at any instant the temperature in the various regions of the mass constituting the charge of the boxes.

This last condition may be realized quite well by placing a tube of iron along an axis of symmetry of every cementation box in such a way that the two open ends of the tube pass tightly through the walls of the box and project outside of it.

A thermo-electric couple, whose junction, suitably insulated, is placed successively at various points of the tube, permits then of determining the temperatures of the various "strata" of the mass, in each of which, for reasons of symmetry, the temperature must be nearly constant. Nevertheless, the placing of such tubes is not always possible; as happens, for example, when pieces of steel of considerable dimensions are to be placed in the boxes. And in any case the joints between the tube and the walls of the boxes very quickly become loose, giving admission to air, which is very harmful to the success of the cementation. This results in greatly shortening the normally brief "life" of the cementation boxes, and therefore in enormously aggravating the most serious disadvantage of the processes of cementation using boxes.

Nor can the theoretically perfectly logical and very ingenious solution proposed by Grenet[1] be regarded as practical. It consists in "heating the boxes in a continuous furnace whose temperature rises sufficiently slowly so that the boxes may be considered practically to be in temperature equilibrium with the furnace." Grenet proposes to obtain such a result by means of furnaces of an elongated form, whose ends are kept at a temperature considerably lower than that of the operation at which the cementation is to be effected; the boxes would be introduced into the furnaces successively "in series" from these ends, and gradually pushed toward the hotter parts of the furnace.[1]

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[1] L. Grenet, *Trempe, recuit, cémentation et conditions d'emploi des aciers* (Paris, Béranger, 1911, p. 214).

Then "the law of the cementation would be deduced from the velocity of the circulation of the boxes and from the law of the temperature of the furnace."

But Grenet himself recognizes that "this system would have the disadvantage of increasing the duration of the cementation, and, moreover, like all apparatus for continuous operation, such a furnace would not lend itself to enormous variations in the cementation. If in the same furnace could be placed two series of boxes, which were made to proceed with different velocities, there could be obtained two thicknesses of cementation, which in many cases would be sufficient." It is evident that such a procedure can not be applied in the very great majority of cases.

From what has been just said, and from the data reported in the preceding chapters, it is easy to understand how, in almost all of the cases which present themselves in the technology of the processes of cementation based on the use of solid cements in the boxes, a *precise* and *truly efficacious* control of the temperatures of cementation is practically impossible.

Ordinarily, makers of machine parts limit themselves to measuring repeatedly the external temperature of the boxes during the entire operation and from the results of such measurements it is generally held, in truth with a certain ingenuousness, that it is possible to deduce, "with the aid of long practice," some useful indications as to the course of the heating within the boxes.

The pyrometers most frequently employed for this use are the Le Chatelier thermo-electric couple and Féry's optical pyrometer.[2]

The use of these apparatus is now very extensive in all branches of metallurgical technology, and is to-day familiar to every one;[3] we limit ourselves to referring to the way they are generally used for the measurement of the temperature of the cementation boxes.

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[1] It is well known that an analogous procedure is used to obtain the "gradual" heating of steel objects of large dimensions which are to be hardened "in series;" for example, for the hardening of projectiles of large caliber.

[2] In some works Seger cones are used, placed at various points of the laboratory of the furnace. Usually, cones of two series are employed simultaneously; those melting at a lower temperature (usually 25° C. below the normal temperature of the cementation) are introduced from time to time to determine if the temperature has reached the minimum required, while those melting at a higher temperature (about 25° C. above the normal temperature of the cementation) are left constantly in the furnace to make sure that the temperature in it never exceeds the pre-established maximum. The insufficient precision and the slight certainty with which temperatures can be measured by means of the Seger cones render absolutely inadvisable the method of control just referred to.

More precise results are obtained with the Siemens calorimetric pyrometer, but every measurement with this apparatus requires some delicate manipulation which renders its frequent use not very convenient.

[3] On apparatus for measurement of high temperatures consult Le Chatelier and Boudouard, *Mesure des températures élevées;* Roberts-Austen; *Introduction to the Study of Metallurgy;* C. R. Darling, *A Practical] Treatise on the Measurement of High Temperatures,* London, 1911.

In using the Féry pyrometer (direct vision or telescope) it suffices to point it directly at the wall of one of the boxes, and it is desirable that the apparatus should be focussed on only a single one of the boxes, so as to avoid the possibility that in the space between the two boxes might appear a section of the wall of the furnace hotter or cooler than the boxes themselves. The same observations hold for the use of other optical pyrometers, such as that of Le Chatelier, Wanner, etc.

When it is desired to make direct precise measurements with the Le Chatelier thermo-electric couple (platinum against rhodium-platinum alloy with 10% rhodium), "spies" are used, consisting of cubes of soft steel of various dimensions, according to the dimensions of the boxes and of the laboratory of the furnace. Usually "spies" of 50 to 80 mm. (2 to 3.2 inches) to the side are used. The cube is traversed by a hole of sufficient diameter so that the end of the iron tube forming the guard of the thermo-electric couple can be introduced into it. Usually a "spy" is placed on every box, so arranged that the hole is directed toward the door of the furnace. In this way it is easy to introduce successively the end of the couple into the various "spies," and to thus follow accurately the variations in the external temperature of each box.

It is well known that many makers place on the market thermo-electric couples already mounted in iron guards filled with insulating refractory material and furnished with a handle with binding screws to which are fastened the copper wires which lead to the galvanometer. But experience shows that these guards are too "perfect" for practical uses. First of all, the thermo-electric couple is fixed in them too rigidly, so that a slight bending of the guard almost always results in wrenching off of the wires of the couple.

Moreover, the replacement of the external iron tube, also carefully fixed to the other parts, is difficult, so that in practice where this substitution is necessary frequently, especially where the instrument is used in an oxidizing atmosphere, it is equivalent to remaking the whole apparatus. Finally, the necessity of not having to change too frequently the various parts of a complicated and delicately set up apparatus entails having to make either the iron guard tube or the refractory insulating material quite thick, and for this reason the couples thus mounted follow slowly and with considerable lag the variations in the temperature of the furnace.

For all these reasons it is better to use a much simpler protecting tube, formed of an iron tube (usually of an external diameter of 15 to 20 mm. (0.6 to 0.8 inch) and 1 to 3 mm. (0.04 to 0.12 in.) thick) in which is placed a porcelain tube, closed at the end corresponding to the closed end of the iron tube. In the porcelain tube, whose external diameter must be 3 to 5 mm. (0.14 to 0.20 in.) less than the internal diameter of the iron tube, the thermo-electric couple is placed, one element being insulated by making it pass through a series of fine porcelain tubes 3 to 4 mm. (0.09 to 0.16 in.) external diameter. The ends of the couple which issue from the tube are fixed to two binding screws carried on an insulating ring, which is attached with a simple pressure screw to a point of the protecting tube itself; to these binding screws are fastened the two copper wires which lead to the galvanometer. In this way all the parts of the apparatus are completely independent of each other, so that each one of them (and especially the iron tube) may be easily and rapidly replaced when it has deteriorated. Moreover, any bending, even considerable, of the iron tube has no other effect than that of breaking, often at various points, the enclosed porcelain tube, but the various pieces of the latter continue acting as insulators, and in any case the thermo-electric couple does not suffer at all. Moreover, the thermal insulation of the couple is thus reduced to a minimum.

The measurement of the real temperature of the cementation is much easier and more precise when liquid cements are used, for the convection currents enormously facilitate rapid attainment of temperature equilibrium throughout the mass of the fused cement and the steel pieces immersed in it.

The form of the furnaces usually employed for cementation with liquid cements renders very suitable the use of a protecting tube bent to a right angle for the protection of the thermo-electric couple. Such a form of guard tube, in fact, has the advantage of bringing the binding screws constituting the "cold junction" of the couple outside of the space immediately above the furnace, a space where the hot and corrosive vapors which are evolved from the fused salt bath collect. With a straight guard tube the binding screws would necessarily be in that situation. Moreover, it is evident that a straight guard, having to be very long to carry the cold junction binding screws to a sufficient distance from the bath, is in the way in the operations of charging and discharging the pieces in the cementation bath; operations which must necessarily be made from the upper surface of the bath.

There are on the market thermo-electric couples mounted in guard tubes bent to a right angle, but they present, to a still greater degree, the same disadvantages which I have already enumerated for the straight guards.

On the other hand, it is easy to set up a considerably simpler system, analogous to that which I have already described in the case of the straight guard and which presents, notwithstanding the bend at a right angle, the same advantages (and especially the same facility of mounting and dismounting and the same independence of its elements) referred to for the preceding case.

Fig. 153 represents schematically the vertical section of the guard tube for the thermo-electric couple immersed in the cementation bath. The tube with square bend is obtained by removing the greater part of the wall of the straight tube between two generatrices about 90° distant from each other and bending the remaining part *O* outwardly. It is then easy to mount the couple throughout the whole lower section *LB* in the same way as I have already indicated for the straight guard by introducing into the iron tube the porcelain tube *B* and in this the thermo-electric couple, one wire of which is insulated by means of the usual smaller porcelain tubes. At *E* the couple is bent, the two wires being insulated with porcelain beads, and made to pass into the horizontal arm of the guard, being insulated with two glass tubes. The ends of the two wires of the couple are fastened in the usual way to the two binding screws *H* and *G*. At the various joints a little asbestos fiber can be introduced to better keep in place the different pieces.

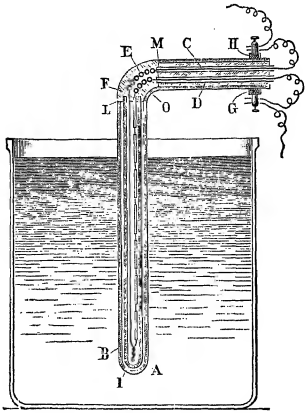

FIG. 153.

This system of mounting the couple is extremely simple and cheap and that which in practice gives the best results and guarantees a longer life of the couple.

For the control of the temperatures in cementation with liquid cements, usually no other pyrometer than the thermo-electric couple is employed.

In cementation with gaseous cements the measurement of the temperature made *directly* on the pieces subjected to the treatment, while it would be easier because the pieces are not surrounded by any solid substance, is hindered, on the other hand, by the necessity of keeping the cementation chamber perfectly closed, so as to avoid entrance of the air or of the gases in the laboratory of the furnace. This necessity excludes, first of all, the possibility of using an optical pyrometer for the measurement of the temperatures *in the interior* of the cementation chamber, and renders it necessary, for making such a measurement with a thermo-electric couple, to arrange one or more metallic guard tubes *soldered* to the walls of the chamber, and placed in such a way that they reach the point of the chamber at which the exact measurement of the temperature is most important. The inside of these guards must communicate with the exterior by means of an opening through which the two insulated wires constituting the thermo-electric couple can pass, but must in no way communicate with the interior of the cementation chamber. If such a communication should exist, not only might the gases of the laboratory of the furnace or of the outside atmosphere penetrate into the cementation chamber, mixing with the carburizing gas and weakening its carburizing efficacy, but the metal thermo-electric couple, coming in contact with the carburizing gases, would be gradually altered, becoming brittle and ceasing to give exact temperature indications.

The difficulty of realizing in practice the conditions just referred to, especially when the cementation chamber is movable,[1] results in the majority of cases in only the *external* temperature of the cementation chamber being measured. In these cases the measurement of the temperature is made according to the same rules as hold for the measurement of the temperature of the ordinary cementation boxes, except that in the case of the gaseous cement the absence of a mass acting as an excellent thermal insulator (such as that constituted for the most part by the solid cements) results in the equilibrium between the external temperature and that within the cementation chamber being reached in a considerably shorter time, so that the errors arising from the imperfect knowledge of the law of the propagation of heat from the periphery to the center of the mass contained in the cementation chambers are, all other conditions being equal, markedly diminished.

When the cementation is carried out with mixed cements (solid and gaseous) under the conditions already indicated in detail, the direct measurement of the *true* temperature of the cementation can be effected in a considerably easier and more certain way than in the cases in which the solid cements or the gaseous cements are used separately. And this for the following essential reasons:

1. Contrary to the ordinary solid cements, the solid constituent of the mixed cement (usually "granular" wood charcoal) forms a mobile mass endowed with very slight consistency, and these qualities are in no way diminished during its use, for the granular carbon of the mixed cement is simply "poured" like a liquid on the pieces to be cemented and it is in no wise necessary to compress it around them to insure contact with the surface of the steel. The result of this is that it is easy to introduce the iron tube containing the suitably insulated thermo-electric couple *at any point* of the mass of granular carbon and thus to measure the true temperature of cementation without the necessity of fixing any special tube or other article into the cementation chamber.

2. Contrary to what happens in the use of the ordinary gaseous cements, the gaseous constituent of the mixed cement (usually a mixture of carbon monoxide and of carbon dioxide) does not circulate freely in the spaces between the various pieces of steel in the cementation chamber; it is, on the contrary, forced to circulate in the very small interstices which separate the grains of carbon, permeating the mass of this carbon. Under such conditions, the carburizing gases encounter appreciable friction in the mass

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[1] As, for example, in the Machlet furnaces, referred to on pp. 287-293.

through which they have to circulate, and they escape from it only very slowly, even when the external surface of this mass comes in contact with a gas of composition different from that of the gases which permeate it. It follows from this that in cementation carried out with the mixed cements the cover of the cementation chamber can be opened to introduce the pyrometer into the mass within it without the external gases being able to penetrate into it to an appreciable depth and reach the steel pieces. This penetration is also retarded by the ascending current of carburizing gases which circulate slowly in the apparatus.

3. Contrary to practice with the ordinary solid cements, where the charge must be made cold on account of the necessity of gradually charging the steel pieces and the cement, the mixed cements permit of introducing the charge quite hot, so that, up to the beginning of the operation, the temperature is almost uniform throughout the whole charge, and such that the process of carburization begins at once. This fact permits of timing with precision the real period of the cementation for the whole charge, and renders it unnecessary to carry out the measurement of the temperature at more than a few points in the cementation chamber.

It follows that the practical measurement of temperatures in operations carried out with mixed cements approaches those where liquid cements are used rather than those followed for gaseous cements or solid cements. In fact, for the mixed cements also, the best way of effecting control of the temperature consists, as we have seen, in "immersing" the junction of the thermo-electric couple (suitably protected) directly in the mass contained in the cementation chamber.

As regards the control of the temperatures of quenching, there is no need of using special arrangements and apparatus. As for the apparatus designed for the quenching itself, so also for those designed for the control of the temperatures at which it is effected, they do not differ from those which are ordinarily used for the quenching of any other kind of steel objects.

The same observations hold as regards the control of the temperatures of tempering and of annealing of cemented and hardened pieces.

§ 3. CONTROL OF THE COURSE OF THE CARBURIZATION

Only when cements of a simple, perfectly defined and well-known chemical nature are used, and the cementation is carried out under conditions which are well defined and can be continuously controlled with exactness, is it possible to obtain satisfactorily cemented zones of the desired type. We have seen that such a result can be obtained when certain gaseous or mixed cements are used and the temperature of the cementation, the pressure of the carburizing gas, the velocity with which this gas circulates in the cementation chamber, etc., are carefully controlled.

In the majority of cases these exact controls are not practically possible, and a pre-established result can be obtained with certainty only by following closely the carburization of the pieces by means of the frequent examination of one or more test pieces of this steel, placed in the cementation chambers. As to the method of placing the control specimens in the solid cement of the ordinary boxes, sufficient directions have already been given (see p. 275).

In cementation with gaseous cements, the control of the course of the carburization by means of the examination of the test pieces is most difficult in practice, owing to the necessity of opening the cementation chamber during the operation to remove the test pieces, and I have already enumerated in the preceding pages, in connection with the measurement of temperature, the disadvantages of this opening.

Where the cementation is carried out with the liquid or mixed cements, the control is exceedingly easy, for in these cases a rod of steel can, without any inconvenience, be immersed in the cement and then removed for examination as many times as may be considered desirable, without any harm at all to the regular cementation of the other steel objects.

I have already pointed out how the method generally used for the examination of the control specimens, consisting in quenching them, breaking and examining their surface of fracture, can give only uncertain and incomplete results, and this because of two reasons:

1. The peripheral "fine-grained" region which appears on the surface of fracture of a cemented and hardened specimen,[1] and on which the determination of the depth of the cementation is frequently based, in no way corresponds to a region in which the concentration of the carbon exceeds or at least equals a *well-defined* value; this is shown by the fact that a same cemented piece (in which the uniformity and the thickness of the cemented zone have been controlled by precise means, such as chemical analysis or microscopical examination), when quenched under conditions differing only slightly, and broken in different ways (for example, with different velocities of shock) presents in its surface of fracture "fine-grained" peripheral zones of different extents. It is clear, therefore, that the examination of the fracture can furnish a measure of the *depth* of the cementation only to a very rough approximation.[2]

2. The examination of the surface of fracture of a cemented and hardened piece of steel can furnish no indication as to the maximum concentration of the carbon in the cemented zone and, still less, as to the variations in the concentration of the carbon (or the "distribution" of the carbon) in the vari-

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[1] As is well known, for a cemented zone with 0.9% of carbon, obtained in an ordinary soft steel, the temperature of heating best adapted to show the fineness of the "grain" by means of quenching in water is between 750° and 780° C., and varies according to the dimensions of the piece which is hardened, the temperature of the water, etc.

[2] As a confirmation of these assertions, I think it well to copy here some numerical

ous layers of the cemented zone. The knowledge of these last data is often more useful than that of the actual depth reached by the cementation.

From all this follows the necessity of having recourse to more precise means of examination whenever sure and complete data as to the course of the cementation are to be obtained from the examination of the control specimens.

Also, in view of the frequency and the rapidity with which the observations on the control specimens must be made, it is absolutely impossible to have recourse to chemical analysis, especially because it would give complete results only when made on various successive layers of the cemented zone.

Rapid and almost as precise results are given, on the other hand, by the microscopic examination of the cemented control specimens, allowed to cool slowly. This examination, which is always made on a plane section normal to the surface of cementation, presents no difficulty and requires but a few minutes.

The usual reagents used in metallography for etching carbon steels[1] show up very clearly the three constituents, from the relations of which the carbon content of the steel examined can be at once deduced, coloring the pearlite (or, as the case may be, the sorbite) a dark brown, and leaving brilliant the ferrite, and the cementite, which are then easily distinguished from each other by the form of their structural elements. Hence, to obtain

data reported by A. Portevin and H. Berjot (see *Revue de Métallurgie; Mém.*, 1910 pp. 73-74).

Depth of cementation measured with the microscope on non-quenched and polished specimens (mm.)	Depth of cementation measured on the same specimens, quenched and broken (mm.)
0.50	0.45
0.84	0.65
0.90	0.72
1.25	1.10
1.50	1.17
1.92	1.72
2.30	1.65

The corresponding pairs of figures in the two columns refer to the same specimen.

The effect of the conditions of quenching on the measurement of the depth of the cementation based on the examination of the surfaces of fracture may be seen from the following table, the values of which all refer to the same specimen (see Portevin and Berjot, *loc. cit.*).

Condition of execution of measurement	Depth of cementation (mm.)
On non-quenched and polished specimen..............	1.62
On specimen quenched at 700° and broken.............	1.57
On specimen quenched at 800° and broken.............	1.92

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[1] The most frequently used of these reagents are a 5% alcoholic solution of picric acid and a 5% solution of nitric acid in amyl alcohol.

precise data as to the concentration of the carbon it is not necessary to extend the polishing until the disappearance of the last striæ, for these do not so mask the structure as to prevent a correct estimation of the relations between the areas occupied in the section by the various constituents. Under these conditions the polishing does not require more than two or three minutes. If we add the time necessary to cut from the control specimen a piece of the size adapted for the metallographic examination, and the few seconds necessary for the microscopic examination, it is seen that for the whole test not more than four to five minutes are required.

The numerous examples which I have reported in the first part of this volume show the precision and the clearness of the data which the metallographic examination of the cemented and non-tempered pieces can furnish, both as to the maximum concentration and as to the distribution of the carbon in the cemented zones. It suffices to use, for this examination, a microscope supplied with an exact micrometric apparatus.

It is necessary to point out, however, that since the deductions from the control specimens have no absolute value if the composition of the steel of which they are made is not identical with that of the objects whose cementation is being controlled, the microscopic examination of the control specimens will cease giving precise and absolute results when various special steels are being cemented. All such steels preserve, after the heating, the martensitic or polyhedric structure of γ-iron. In the majority of these cases, however, the examination of the surface of fracture also does not furnish clear or precise data.

An experienced eye can also obtain satisfactory data of precision as to the depth of the cementation and the concentration and the distribution of the carbon in the cemented zones from a simple examination with the naked eye of the plane sections of the control specimens, polished and etched with the 5% alcoholic solution of picric acid. In the section thus prepared, examined obliquely under an intense light, there appear most clearly and in strong contrast with the brown areas of the pearlite, the gleaming needles, of the cementite and the more extended clear masses of the ferrite. Especially clear to the naked eye appear the eutectic zones, of compact pearlite, and the lines of abrupt junction (corresponding to sudden variations in the concentration of the carbon) between these zones and the contiguous hyper-eutectic or hypo-eutectic zones.

It is clear, however, that a correct estimate of the various concentrations of the carbon and the thicknesses of the differently carburized individual layers can be obtained only by means of the microscope and with the aid of micrometric gratings which permit of determining such small lengths and of measuring with good approximation the areas occupied in the section of the steel by the individual constituents.

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§ 4. CONTROL OF THE CEMENTED PRODUCTS

In the greater number of cases the cemented pieces are intended to be used only after quenching, so that almost always, after the control of the course of the carburization with which we have dealt in the preceding section, the cemented piece is not subjected to any direct tests until it has undergone all the further heat treatments designed to make it suitable to be put into use. It is only in exceptional cases that a direct examination of the piece as it issues from the cementation chamber is undertaken.

When having many identical pieces (for example, bolts, dies, small axles, etc.) to be cemented under identical conditions, one is removed from time to time to examine its fracture after quenching, polishing and etching a section, the pieces thus examined become useless and can be considered only as true control specimens proper. The only cases in which a direct control of the result of the cementation on the cemented but not hardened pieces is desirable are those in which a deficiency or an excess in surface hardness in analogous cemented and hardened pieces has been observed, and it is desired to find its cause by separating the control of the effects of the cementation from that of the effects of the quenching. These latter tests, as is well known, depend on the dimensions and on the form of the object under consideration, and they can not, therefore, be controlled with certainty by examining a specimen different in form and dimensions from those of the object dealt with.

If the piece on which it is desired to control the result of the cementation must not be altered, and no part of it can be removed, it is clear that the control can not extend beyond the surface layer of the metal. In this case, the only control possible consists in polishing a more or less extended section of the surface of the object, etching it with one of the usual reagents and examining it under the microscope, so as to determine the carbon content of the surface layer of the object.

If, on the contrary, it is possible to remove from the object which it is desired to examine, without rendering it useless, a piece of sufficient dimensions so that it will include all or part of the thickness of the cemented zone, it is clear that the control of the cementation can be carried out with the methods referred to for control specimens.

The interpretation of the results furnished by the various methods (and especially by the micrographical method) has already been dealt with at length in the first part of this volume, where especial emphasis was placed on the strict relations which exist between the distribution of the carbon in the cemented zones and the phenomena of "exfoliation" which may manifest themselves in these zones after quenching.

The control of the superficial carburization, made directly on the cemented pieces in the manner indicated, may give useful indications where extremely thin cemented zones are dealt with, like those which we have seen can be obtained in the processes of rapid cementation, for example, with fused potassium ferrocyanide. In such cases, in fact, it is not possible to require one rather than another distribution of the carbon in the successive layers of the cemented zone, and the value of the result obtained depends only on the concentration reached by the carbon at the external surface of the cemented piece.

§ 5. CONTROL OF THE CEMENTED AND HARDENED PRODUCTS

The methods for the control of the cemented and quenched products may be collected in two groups. The first of these groups includes the methods whose application renders the piece examined useless, so that these methods can be applied only to a specimen subjected to treatments as nearly identical as possible with those undergone by the pieces which it is desired to control, or to one or more of these pieces themselves when it may seem convenient to prepare and treat a certain number of pieces designed especially to serve as test pieces and therefore to be put out of commission. It is clear that the second procedure, in which the pieces utilized as control specimens are *identical* with the pieces which are really to be used, can furnish considerably more precise indications than that based on the examination of specimens of different form and dimensions, but it is also clear that this procedure can be applied in practice only when it is a question of controlling not very expensive pieces, manufactured and treated in series.

The methods which may be collected in the second group are those which can be applied directly to the cemented and hardened pieces without their being made useless.

Among the methods of the first group, we will recall those designed to verify the effects of the various heat treatments on the mechanical properties of the "core" of the cemented pieces; those designed to verify the course of the variations which the hardness of the steel presents at various depths, the superimposed effects of the cementation and of the hardening; those designed to find the causes of the brittleness of a cemented piece, etc.

To the second group belong the methods designed to determine the mineralogical hardness of the surface of the cemented and hardened piece and to control the efficacy of the means of protection applied to the parts of the steel pieces which are not be be hardened even at the surface; those designed to determine the brittleness of the cemented zone and to furnish approximate indications as to the thickness of this zone; those designed to learn whether the insufficient mineralogical hardness of the surface of the cemented piece is due to defects in cementation or in quenching or to a superficial decarburization manifesting itself during the treatments which followed the cementation, etc.

We have already seen that one of the most serious and most frequent of the disadvantages which manifest themselves in cemented pieces is the brittleness of the internal part, or "core" of these pieces, which the carburizing effect of the cement must not reach.

We have also seen already that, whether the cause of this phenomenon is chemical or whether it lies simply in the prolonged heating at a high temperature to which the steel pieces are subjected during the cementation, we can study out on perfectly rational bases the heat treatments by means of which the brittleness of the core of the cemented pieces can be reduced to a minimum while the maximum hardness is obtained in the peripheral zone.

Recognizing the importance of the result which it is desired to obtain and the delicacy and the precision with which these heat treatments must be conducted, the importance is evident of carrying out an exact control to find with certainty if there have really been obtained the mechanical properties which it was desired to impart to the "core" of the cemented pieces by these treatments.

For the control of the tenacity of the metal constituting the core of a cemented piece, there exists no method which permits of making the test without rendering useless the piece examined.

The simplest, but not sure, means of judging of the tenacity of the core of a cemented piece consists in breaking it and examining the appearance of the surface of fracture.

It is well known that a brittle soft steel presents, under such conditions, a "grained" surface of fracture, while for a tough steel this surface has the characteristic appearance usually designated by the term "fibrous" or "nerve structure."

A first cause of the insufficiency of this method of control lies in the fact that the results which can be obtained by it depend only on the personal judgment of the observer, and can not be represented in any way by means of figures.

But there is another fact which proves even more the imperfection of the method just referred to, even when we do not take into account the errors which may result from an inexact estimate of the observer; the appearance of the surface of fracture varies to a very marked degree with variations in the way in which the specimen is broken. Thus, it is easy to observe that the fracture of a specimen (treated in a perfectly homogeneous way) at various points near to each other presents a different appearance according to the way in which the fracture is produced and according to the direction of the surface of fracture. In general, it may be stated that a fracture produced by applying a bending force increasing gradually and slowly, or by applying a series of successive forces, tends to increase the "fibrous" structure, while a surface obtained by suddenly applying a very strong force (dry blow) tends, in general, toward a "grained" structure.

Fig. 154, taken from the interesting memoir of Guillet which I have cited several times,[1] places these facts well in evidence.

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[1] *Le Génie Civil,* 1911, II, p. 286.

The various surfaces of fracture reproduced in the figure, some of which are distinctly fibrous while the others are "grained," are, in fact, obtained by breaking in different ways at different points, quite near to each other, the same bar of cemented soft steel.

The examination of the "fiber" of the surfaces of fracture may have some practical value when always carried out under identical conditions, by the same workman who has taken care to find out, on the basis of preliminary tests, what structure ought to be observed for each form of specimen and for each kind of steel to obtain good results.

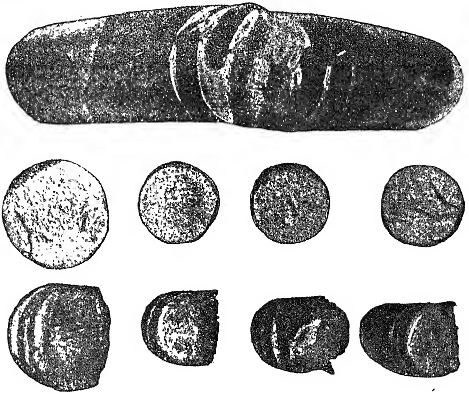

FIG. 154.

Another criterion quite frequently followed in practice to judge of the greater or lesser brittleness of the "core" of a cemented specimen, consists in observing the maximum angle through which the specimen can be bent before breaking, under the action of one or more shocks or of a force applied gradually.

But the results which can be attained with this method are also very far from having any absolute value, for the following reason: As is well known, the cemented and hardened zone, being composed of a steel incapable of undergoing appreciable elongation under tensile forces, quickly splits at the first deformations undergone by the specimen subjected to the bending test. These cracks, which show especially (as appears clearly in Fig. 154) in the convex part of the bent specimen, by propagating themselves, even slightly, into the mass of the soft metal constituting the core of the cemented steel produce there the special effects of a series of very sharp cuts. And it is well known how such cuts lower enormously the resistance to bending and to shock of the metallic piece in which they are made, giving rise to a kind of phenomenon of "inoculation" of the surfaces of fracture which are produced there as the result of the mechanical force.

For this reason, the method of applying the force to produce fracture by bending cemented specimens influences the behavior of these specimens to an enormously greater extent than in the case of homogeneous specimens.

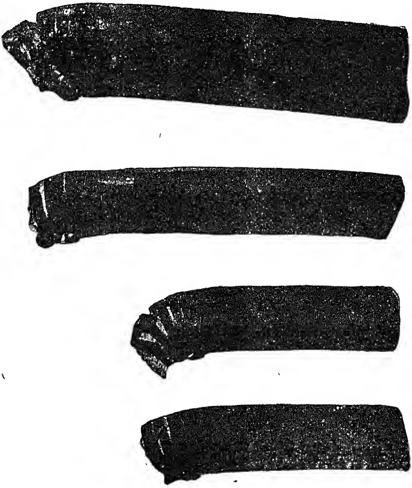

FIG. 155.

An example of the different behavior of a cemented and quenched specimen under the action of shocks applied under various conditions is furnished by Fig. 155, also taken from the same memoir of Guillet just cited. The two fractures shown in the figure were made at two points of a same cemented bar, not more than 10 cm. distant from each other. The first (between the two pieces shown at the bottom of the figure) was obtained by a series of weak shocks and was produced only after the specimen had undergone marked deformation. The second (between the two pieces shown in the top part of the figure) was, on the contrary, obtained with strong and sudden shocks; it is clearly to be seen that the fracture was produced without any previous marked deformation of the specimen.

The only manner of determining with certainty and of expressing in numbers the brittleness of the core of a cemented piece is the shock test, carried out under the well-known "normal" conditions; that is, by breaking a bar of well-defined form with a single blow of a mass moving with a definite *vis viva*, and measuring the residual *vis viva* of the striking mass after the breaking of the specimen. The determinations just referred to can be carried out with various apparatus, such as the Charpy pendulum, the Fremont hammer and the Guillery fly-wheel apparatus.

In the case of the cemented steels *it is absolutely necessary* that the normal bar which is to be subjected to the shock test *should be taken entirely from the core of the cemented specimen* and should contain no part of the carburized zone. This is for two essential reasons:

First of all, in the well-known special form of the normal test piece now generally adopted,[1] the part of it in which the fracture must begin as the result of the shock of the striking mass of the test apparatus is precisely that which, owing to its form (hole of 4 mm. in diameter and 30 mm. in depth), is always cemented under conditions very different from those average ones under which the objects have been cemented whose mechanical properties are to be judged.

In the second place, the presence in the test pieces to be subjected to the shock test of a highly carburized and hardened external zone gives rise to the phenomena of "inoculation" of the surfaces of fracture already referred to and reduces, therefore, the apparent tenacity of the metal constituting the core of the cemented piece to an extent always large but which is most variable, and which depends, more than on the nature of the metal used, on a great number of small causes which it is most difficult, if not impossible, to take into account in practice.

When cemented objects are manufactured whose mechanical properties it is desired to make absolutely sure, the test of the brittleness of the metal constituting the core of the cemented and hardened pieces must be repeated every time that a steel of a new make is used or that it is desired to introduce modifications of some importance in the heat treatment of the cemented pieces.

A second point which we have seen is of importance for the quality of a piece of cemented steel is the variation in the hardness of the steel constituting the carburized zone, as we pass through successive layers of this zone. Characteristic variations in the hardness of a cemented and quenched piece may depend on the variations in the concentration of the carbon in the cemented zone as far as they are due to the manner of conducting the cementation and also on the manner in which the subsequent heat treatments of the cemented piece have been conducted. The examination of the merely cemented control test pieces can not alone suffice, therefore, to establish the cause of a definite "distribution of the hardness" in the cemented zones of objects subjected later to further heat treatment. Further heat treatments may not only make the "distribution of the hardness" vary on account of the fact that they exercise their action with different efficacy at different depths in the mass of the steel, but also because their application, carried out under definite conditions, may also cause the distribution of the carbon to vary, within quite wide limits, in the cemented zones. This is caused especially by the heat treatment favoring or hindering the processes of segregation occurring during the cooling of the masses of steel of non-uniform composition.

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[1] As is well known, this is the test piece proposed by Charpy. It is a prism 160 mm. long with square section of 30 mm. to the side, with a cylindrical hole 4 mm. in diameter, of which one of the generatrices coincides with one of the two minor axes of symmetry of the prism; the metal which remains on one side of the hole is cut with a saw in the shortest way, and therefore normally to one face. On the side of the cut the bar is supported by two knife edges placed at distance of 120 mm., while the blunt knife edge, connected to the striking mass, strikes the opposite face, corresponding to the axis of the hole.

It follows that it is necessary to complete the examination of the characteristic properties of the successive layers of the cemented zones, carried out on simply cemented control test pieces, by a similar examination of the cemented and hardened zones.

In general, this examination also renders the piece on which it is carried out useless, so that, if we except the cases just referred to, this examination is made on test pieces cemented and hardened under conditions as similar as possible to the treatment of those which it is desired to control.

In any case, it is necessary, first of all, to make a plane section normal to the surface of the piece. This section, recognizing the hardness of the cemented and quenched metal, can be made only by means of a disk of abrasive material (for example, carborundum) revolving with a high velocity and constantly fed with an abundant stream of cold water. This last precaution is absolutely necessary to prevent the great heating from altering the effects of the original thermal treatment to which the cemented piece was subjected.

When deep cemented zones are dealt with (as, for example, those which are obtained in ordinary ship armor) it is easy to control directly on the plane section of the cemented zone the hardness of the steel of the various layers by using center punches of a steel of definite composition, hardened and tempered under well-defined and constant conditions. By always using punches identical with each other, even in form, and always delivering the blow of the hammer in the same way, the examination of the stamp left by the punch on the plane surface of the cemented steel and that of the deformations or the fractures suffered at the same time by the point of the punch permit of obtaining sufficiently approximate indications as to the mechanical properties of the steels tested. These indications, however, have an exclusively relative value and depend to the greatest degree on the personal factor of the experimenter.

Considerably more precise results, possessing a certain absolute value and which can be expressed in figures, are obtained by substituting, under the same conditions as just indicated, for the test made with the punch the hardness tests carried out with the well-known apparatus of Brinell or of Shore. However, the first method—that of Brinell—can furnish precise results only for the layers of medium hardness, so that the data which can be obtained with it for the surface layers of the cemented zones can not be rigorously compared with those which it furnishes for the deeper layers. The data obtained by the Brinell method for the harder parts of the cemented and tempered zones (for example, above the hardness number 600) will, however, have real practical value if considered solely in their relations to each other. As to the results which are obtained with the Shore sclerometer, there are difficulties in practice in obtaining them under conditions such that they are rigorously comparable with each other.

It is clear that no one of the three sclerometric methods just referred to is applicable in practice when the thickness of the cemented zone is less than 4 or 5 mm. This is true in the large majority of the cases in practice, but interesting indications as to the "distribution of the hardness" in the cemented and hardened zones can then be obtained by using the Martens diamond point sclerometer.

Finally, useful indications can often be secured, especially as to the *causes* of a given distribution of hardness, by means of the microscopic examination of sections made across the cemented and hardened zone. And it is further evident that this means of investigation is the only one which permits of distinguishing if a definite variation in the hardness is due to a variation in the concentration of the carbon or to a difference in the conditions of hardening. I cannot enter here into details as to the method of interpreting the results of the micrographic examination of the cemented and hardened pieces, but it is clear that this interpretation does not require any special knowledge other than ordinarily used in the microscopic examination of any other kind of hardened steel. The appearance of the martensite and the degree of its transformation into its successive segregation products, from osmondite to lamellar pearlite, permit of judging with certainty of the effects produced by the hardening and by the recovery in each of the individual layers of the cemented zone and of thus separating the variations in the hardness due to these effects from those due to variations in the concentration of the carbon. The disappearance of the constituents characteristic of γ-iron steels, a disappearance which (as is well known) rarely manifests itself in practice for carbon steels but easily occurs for a large number of special steels of low transformation temperature, permits of distinguishing easily if the phenomena of deficient hardness or of excessive brittleness which manifest themselves throughout *a whole layer* of the cemented zone are due to ill-chosen conditions of quenching or to a local deficiency or excess in carburization due to irregularities in the cementation.

The microscopic examination of the sections of the cemented test pieces, extended to the metal constituting the "core," can furnish very interesting information as to the most suitable conditions for the "regeneration quenching" of this metal.

A detailed study of such observations would present no peculiarity because these observations were applied to cemented steels rather than to homogeneous steels, so that, while it might logically find a place in a general treatise on the processes of hardening, it would be out of place in discussing merely the control of the cemented products, and a study of those of their properties which depend, directly or indirectly, on the cementation.

Among the methods for the testing of the cemented and hardened pieces which can be used without ruining the piece to which they are applied, the determination of the surface hardness of the cemented and quenched pieces is of most practical importance. In the very great majority of cases, the property which it must be sought to obtain, to the maximum degree compatible with a not too excessive brittleness, is "mineralogical hardness" upon the surface of the cemented and hardened pieces. It is well known that this property, which can also be designated as "resistance to abrasion," is measured by the greater or lesser difficulty with which a sharp body, of a hardness markedly higher than that of the surface examined, can scratch this surface.

The method most frequently adopted in works to control the surface hardness of the cemented and quenched pieces consists in trying to attack them with a file with a fine edge. It is easy to understand how such a test is not precise, the results obtained by it depending first of all on the hardness and on the state of the edge of the file, and then on the way of making the test and on the personal equation of the workman in estimating the greater or lesser "bite" of the file on the metal tested. Moreover, the impossibility of representing the results of the test in figures is evident.

Notwithstanding this, the file test is still widely used in practice as being the simplest, and owing to the fact that it does not require the use of complicated apparatus or of precise methods of measurement, it can be entrusted to a workman. To carry out this test, it is desirable to use files of a very fine edge and of as constant a quality as possible. Given the maximum carbon contents and the conditions of quenching which we have seen are to be preferred for the cemented steels, it would be well to use files made of a steel with 0.9–1.0% of carbon, hardened between 780° and 800° C. and tempered toward 200° C.

Data considerably more precise and which can be expressed in figures are obtained with the Martens sclerometer. In works practice, the use of this apparatus presents some disadvantages, first of all because the apparatus is delicate and must be operated with a certain care, and then because the sclerometer, in the form in which it is ordinarily constructed, is not suited for determining the surface hardness of pieces of large dimensions and of complicated form.

This last disadvantage can be eliminated by modifying the apparatus in such a way as to leave a large free space below the diamond point and supplying it with a universal support which will make it easy to fix even large pieces of a complicated form in such a way that the section of their surface at which it is desired to determine the hardness will be about horizontal. It is desirable that this modification should be completed by making the piece to be examined stationary and, on the other hand, making the diamond point move with its load.

It is well known that even when the steel examined is homogeneous throughout its whole mass, the results of the hardness tests made "by abrasion," by one of the methods indicated above, are in no wise connected by simple relations with the results furnished by the other methods of measurement based on the penetration, *without abrasion*, of a hard body into the mass of the steel.

In the case, then, in which the tests above referred to are made on pieces only superficially cemented, so that the action of the hard body penetrating into the steel, transmitted to the soft layers lying beneath the carburized zone, can not be considered as null, the results furnished by the two methods of testing differ from each other to a still more marked degree, because the differences which are present in the case of the homogeneous steels are increased by those due to the mechanical properties of the metal constituting the core of the cemented piece. The cemented layer communicates to this a part of the force exercised by the hard body penetrating into it, a part which is greater the thinner and harder this layer.

It is clear, therefore, that the results of the methods of testing belonging to the second group, especially if considered in connection with those furnished by the methods belonging to the first, must be capable of furnishing, if suitably interpreted, indications as to the depth of the cementation. From this point of view they present marked practical interest.

Among the methods of the second group, there is largely used in practice, to supplement the file test, the penetration test with a punch of definite hardness and form, struck with a hammer.[1] As to the degree of exactness of this method, the observations already made in connection with the file test can be repeated, for it is clear that the results will depend on the hardness of the punch used, on the form of its point, on the force of the blow of the hammer and on the manner of estimating the resistance offered by the metal.

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[1] In the hardness tests with the punch, the workman is strongly advised to protect his eyes, by means of goggles, from the very dangerous splinters of steel which are detached either from the punch or from the piece tested.

Here too, then, it is a question of results which can not be expressed in figures, and which depend to a large extent on the estimation of the workman.

As an approximation, it may be said that in using a punch of ordinary tool steel, hardened at about 750° C. and tempered at about 200° and striking it with medium force, if the surface hardness has been found good by the file test, the fact that the cemented zone is completely perforated by the punch is a proof that the thickness of this zone does not exceed two or three tenths of a millimeter.

Under the same conditions, well-hardened cemented zones of a thickness greater than 0.3 mm. blunt the point of the punch.

The impossibility of giving more precise general rules on these methods of testing is evident. It is certain, however, that by making a series of preliminary tests on cemented zones of a thickness first approximately tested by examination of the surfaces of fracture, and by always working then under identical conditions, using identical files and punches treated in the same way, it is possible to acquire sufficient practice to get quite precise data as to the depth of cemented zones up to a thickness of even 1 to 1.2 mm. For thicker zones there would be needed too large punches, struck with too great a force, to make it possible to practically carry out the test on cemented and hardened pieces of moderate dimensions.

In these last cases, and even for the thinner zones, when it is desired to obtain more precise results, an analogous test may be made under considerably better conditions by comparing the results furnished by the Martens sclerometer (or some other analogous one, such, for example, as that of Turner or that of Jaggar) with those furnished by hardness tests based on the measurement of the resistance to penetration of a sphere (Brinell method) or of a cone (Ludwik method) of quenched hard steel. In this case also, the results furnished by the first method of testing (resistance to abrasion) are independent of the depth of the cemented zone, while the results of the methods of testing of the second group are closely related to this last quantity. Knowing what resistance to penetration corresponds to a definite resistance to abrasion when the steel tested is uniform throughout its whole mass, or is cemented to a considerable depth (7–8 mm.), the difference between the resistance to penetration thus deduced and that directly determined on a cemented and hardened piece can furnish a measure of the depth of the cemented zone of this piece. It is clear that this difference increases, other than with decrease in the thickness of the cemented zone, also with increase in the pressure under which the resistance to penetration is determined. So that, in the case with which we are now dealing, comparable data can be had only on the basis of "hardness numbers" (Brinell or Ludwik) obtained by is not necessary, within certain quite wide limits, for the simple determination of the hardness number of a homogeneous steel.

The fact that there is not known (and probably does not exist) a simple relation between the numbers which represent, for a same homogeneous material, the resistance to abrasion determined with the Martens sclerometer and the resistance to penetration determined with the methods of Brinell or of Ludwik, and that such a relation is not known between the numbers which represent the results furnished by the two classes of methods of testing and the thickness of the cemented zone on which these tests were made, causes the method for the determination of the thickness of the cemented and hardened zone to furnish precise and sure data only by making a large number of preliminary tests on materials analogous to those which are to be tested.

It will be necessary, therefore, to prepare a certain number of test pieces (in the form of parallelepipedons) of the same steel as the pieces that are to be tested, and to cement them to different, exactly controlled, depths. This control can be made by examination of the surface of fracture of the cemented and hardened test piece, but it is preferable to make it on the test piece (heated) by means of the microscopic examination of a section normal to the cemented surface, polished and etched with alcoholic solution of picric acid. In this way can also be estimated the maximum concentration reached by the carbon in the cemented zones, so as to take it into account in the subsequent application of the data obtained.

For every depth of cementation are prepared series of various test pieces, each being quenched under different, well-defined conditions as nearly as possible the same as the various conditions under which the pieces that are to be controlled are to be quenched.

Abrasion tests are then made on the individual test pieces by the Martens sclerometer, and penetration tests by the Brinell or Ludwik methods, the results of each of these being noted and collected in tables. Then, making the same tests on the cemented and hardened pieces which are to be controlled, we look in the tables compiled in the way indicated above for the "abrasion" number nearest to that obtained, for which the corresponding number of hardness to penetration is also nearest to that obtained for the piece which is controlled. The depth of the cemented zone of the test piece to which these two hardness numbers correspond will be the nearest to that of the piece subjected to control.

This method, which in the description appears complicated, is of rapid and easy application when conducted systematically and when series of numerous pieces made of uniform materials and treated in a similar way are to be controlled, since in this case it suffices to prepare a limited number of comparison test pieces.

The indications furnished by this method are precise enough for all practical purposes.

The methods of testing the hardness based on determination of the resistance to the slow penetration of a hard body also furnish, indirectly, interesting indications as to the degree of brittleness of the metal constituting the cemented and hardened zone.

Especially interesting, from this point of view, are the indications which can be obtained by examining the appearance, the dimensions and the arrangement of the cracks which are always produced in the imprint left by the steel sphere used for the Brinell test when this test is made under a quite high pressure. The minimum pressure necessary in order that the observations just referred to may give good results is the higher the deeper the cemented zone. In the cases which ordinarily present themselves in the practice of cementation of mechanical pieces, it is often necessary to reach pressures of 20 to 30 tons; this requires the use of apparatus more powerful than those which are usually employed for the Brinell test (maximum pressure, 5000 kg.).

The brittleness of the cemented zone, determined on the basis just referred to, can evidently not be expressed in figures, and an estimate of real practical importance as to its value can be given only after long experience.

The various methods for the determination of the surface hardness, especially the methods based on resistance to abrasion, enable one to recognize extremely thin cemented zones, and so to control with certainty the efficacy of the means of "protection" applied to the parts of the cemented pieces where it is desired to preserve the original tenacity and plasticity of the metal.

For these purposes the simple file test gives results of sufficient precision and certainty. In some cases, in which special guarantees are required, recourse is had to the Martens sclerometer, or to that of Jaggar, for the testing of the zones protected from cementation.

Where such test has revealed insufficient surface hardness of the cemented and hardened piece, it is still necessary to learn the cause of this fact, in order, if possible, to remedy it in the pieces examined, or to correct the further treatment.

The principal causes of insufficient surface hardness in a cemented and quenched piece may be the following: 1. Insufficient thickness of the cemented zone; 2. insufficient concentration of the carbon in the cemented zone; 3. superficial decarburization of the cemented piece, produced in the course of the heat treatments which have followed the cementation; 4. not sufficiently rapid quenching or excessive tempering.

Let us examine separately the distinctive characters of each of these four cases:

1. We have already seen how the excessive thinness of the cemented zone

reveals itself by the characteristics of insufficient hardness only with the tests made by the "penetration" methods (Brinell or Ludwik), while it does not appear in any way in the "abrasion" tests (Martens, Jaggar, etc.). In fact, the relations between the results of the tests made by the two different methods permit, to a certain degree, of measuring the thickness of the cemented zone.

2. A too low concentration of the carbon in the entire cemented zone is revealed when both the abrasion and the penetration tests give too low hardness values. Too slow quenching or excessive tempering also produce similar effects, but microscopic examination permits of distinguishing the two cases from each other.

3. Superficial decarburization occurs quite frequently, as is well known, in the course of the ordinary processes of hardening, tempering and annealing. It is also well known, however, that, omitting the exceptional cases, in which the heat treatments are carried out without any precaution or those in which the pieces treated are of very large dimensions (armor plates), the decarburized zones, though often having their carbon content reduced to 0.20% and sometimes down to 0.05%, are in general very thin. In ordinary mechanical pieces, hardened and tempered with care, it is rare that the thickness of the decarburized zone exceeds one- or two-tenths of a millimeter. In such usual cases, and whenever the cemented zone is so thick that the decarburization affects less than half of its original thickness,[1] the abrasion test (file, Martens sclerometer, etc.) will give excessively low values as compared with the "penetration" tests (punch, Brinell test, etc.). And, in fact, the relation between the hardness numbers obtained by the two groups of tests will furnish useful indications as to the extent of the decarburization.

Useful indications for the "diagnosis" of superficial decarburization of the cemented and hardened pieces can also be obtained from the comparison of the hardness numbers obtained by the Brinell apparatus and by the Shore scleroscope (resiliometer), respectively.

In fact, while the presence in the hardened pieces of a decarburized zone 0.1 to 0.8 mm. thick does not produce a very marked diminution in the hardness number determined by the Brinell method, the hardness numbers determined by the Shore method on the same pieces come out excessively low.

To show within what limits this phenomenon manifests itself, we give in the following table some experimental data taken from a memoir of Portevin and Berjot.[2] The experiments were made by heating three samples of steel with 1.4% of carbon in an oxidizing atmosphere so as to decarburize them superficially in a manner perfectly uniform for each piece, but to a depth varying from one piece to the other. In each piece there were measured the depth of the decarburization, under the microscope, and the hardness after quenching at 740° C. The results were the following:

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[1] It is clear that when this happens, all the hardness tests will give low values, and the cementation must be considered as having entirely failed.

[2] A. Portevin and H. Berjot, *Expériences sur la dureté des aciers trempés, etc.* (*Revue de Métallurgie; Mémoires*, 1910, p. 63).

No.	Carbon content at surface	Thickness of hypo-eutectic layer in mm.	Thickness of eutectic layer in mm.	Height of rebound after hardening	Diameter of Brinell imprint (10 mm. sphere) (3000 kg. pressure
1	0.85	0.0	0.18	80	2.39
2	0.4	0.48	1.00	41	2.94
3	0.2	0.84	1.50	32	2.89

As is seen, for the extreme values the superficial decarburization has produced a decrease of 17% in the original value of the hardness number determined by the Brinell method, while the corresponding decrease in the hardness number determined by the Shore method reaches 60% of the original value.

The differences between the hardness numbers obtained by the two methods may also be utilized for the measurement of the depth of the *decarburized* zone along lines entirely analogous to those indicated for the measurement of the depth of the *cemented* zones. Here too, as in that case, it will be necessary to make a series of hardness determinations by the two methods on the pieces cemented and superficially decarburized under conditions exactly controlled with the microscope, and, with the data thus obtained, compile comparative tables which are then referred to for the control tests of the cemented and hardened pieces.[1]

Experience shows that this method can furnish very useful results in practice.

4. I have already pointed out how insufficient quenching or excessive tempering have the effect of lowering both the hardness numbers determined by abrasion (Martens) and those determined by penetration (Brinell). When this occurs, only microscopic examination can determine to which of the two causes this is due. It is well known, in fact, that the presence and the state of the martensite (and, really, of γ-iron) and the extent of its transformation into osmondite and into the further products, down to

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[1] The same comparison of the Brinell and Shore hardness numbers must furnish useful indications as to the depth of the cemented zones. This results from the interesting experiments reported by Portevin and Berjot in the Memoir cited. (See especially the data reported on p. 69 of that Memoir.) Not yet having had occasion, however, to make sufficiently extensive series of technical tests on this method, we can not say whether it gives in practice better or worse results than those which are obtained by the method, which we have already extensively tried in practice and which is described in the preceding pages, founded on the comparison between the hardness numbers determined by the Martens sclerometer and those determined by the Brinell method.

sorbite and to pearlite, furnish precise and sure indications as to the "degree" of the hardening and tempering.

It is known, also, that in this case, as in every other case in which metallic alloys in the state of metastable equilibrium are to be examined, it is necessary to use the greatest care in carrying out the grinding and the final polishing of the metallic surface so as to prevent the mechanical action of these operations raising even slightly the temperature of the metal. The surest means of achieving this consists in keeping the metallic surface under an abundant stream of water during all these operations. It is also well to frequently interrupt the grinding and the polishing.

Besides the tests to which I have just referred, the microscopic examination of the surface of the cemented and hardened pieces can also reveal one of the most frequent causes of the brittleness of the cemented and hardened zones. In fact, in speaking of the hardening of the hyper-eutectic cemented zones (such as are the majority of those obtained by the usual processes of cementation), I have pointed out how special precautions are necessary so that the heat treatment may not produce a total disappearance of the laminæ of cementite. It is moreover well known that the presence of these are the cause of great brittleness, the effects of which make themselves felt even in the "core" of the cemented pieces, owing to the phenomenon of the "inoculation" of the surfaces of fracture as the result of the sharp cracks which are produced corresponding to the laminæ of cementite. Now, the microscopic examination very easily reveals the presence of the undissolved cementite.

There remains, then, the control of the *form* of the simply cemented pieces and of those cemented and hardened. This control has great practical importance, in view of the fact that there are quite numerous causes which tend, during cementation and quenching, to produce deformation of the metallic pieces.

We have also seen that this control must be carried out with great care, both on the pieces which have undergone only the first quenching, so as to effect a first approximate rectification, and on those which have undergone the final hardening and tempering, so as to effect final straightening.

It is clear, however, that the methods and the operations for controlling the deformations of the cemented and hardened pieces differ in no way from those usually employed for ordinary mechanical operations on surface plates, gauges, calipers, etc.

It is not possible to establish rules of a general character for the depth of cementation best suited for the cemented zone for a given use. This must be determined on the basis of the known properties which steel assumes as the result of a given carburization and estimated by one who has studied this object in all its practical details. Such a study is made by the mechanical constructor rather than by the technologist dealing with the cementation. The latter must simply place himself in the position of obtaining, with the greatest possible approximation, cemented zones possessing the characteristics required by the mechanical constructor, who alone can know with precision the nature of the service to which the cemented and hardened pieces are to be subjected.

Summarizing, we may say that the methods of control spoken of permit of determining the following principal defects which may present themselves in the cemented and hardened pieces, and, in the majority of cases, of recognizing their causes:

1. Excess or deficiency in carburization.
2. Insufficient protection of the regions which are not to be cemented.
3. Sudden variations in the concentration of the carbon in the successive layers of the cemented zone.
4. Lack of uniformity in the cemented zone.
5. Deformations of the pieces after the cementation and after the hardening.
6. Inequalities in the temperature.
7. Excess or deficiency of hardening.
8. Cracks in the cemented and hardened zone.
9. Brittleness of the cemented and hardened zone (tendency to exfoliation, etc.)
10. Brittleness of the "core" of the cemented pieces.

The causes of these troubles and the means of remedying them are in part extremely easy to perceive; thus, for example, it is hardly necessary to say that when a cemented piece is too soft owing to deficiency of hardening it is necessary to quench it more energetically. In other cases, the observations and tests fully discussed in the first and second parts of this volume are sufficient to reveal their causes and their remedies. To cite two examples, the causes and the remedies of an excess or a deficiency in the concentration of the carbon in the cemented zones are explained by the phenomena of chemical equilibrium during the processes of cementation; and those of an irregularity in the intensity of the cementation in the various parts of a piece, due to irregularities in the heating, are clearly explained by the effects of temperature on the velocity of the cementation.

CHAPTER V

SOME PATENTS CONCERNING PROCESSES FOR THE CEMENTATION OF IRON AND STEEL

In the preceding chapters we have cited several times rules and data contained in some patents. But desiring to limit ourselves to the study of cementation proper, we have cited only patents concerning processes on which quite precise and sure data were known. In fact, with a few exceptions we have limited ourselves to reporting quantitative data whose exactness was based on our own experimental investigations, or because they had been directly observed by us in practice.

But this is possible for only a limited number of the processes of cementation patented in various countries. In the majority of cases, in fact, the descriptions accompanying the claims constituting the essential part of the patents are written with every care to avoid disclosing the best way of usefully carrying out the claims in practice. From the point of view of the inventor it would appear sufficient that a description should contain the correct directions, but mixed with any amount of useless data; so that in case of a legal contest it can be maintained that the correct directions were really given.

We will, however, refer briefly to some patents whose true practical value is unknown to us, either for the reasons just referred to or because, although the descriptions furnished are clear and simple, we have not been able personally to test their results nor to obtain information from any one who has tested them. We will limit this review to reporting from many such a few examples adapted to show some of the directions in which inventors have entered this field.

Many inventors have attempted to increase the activity of the carburizing mixtures by the addition of the most varied substances, in the choice of which it is sometimes difficult to find the guiding principle or any reasoning based on well ascertained facts.

One of the substances whose addition to the cementation powders is most frequently proposed is borax. Thus, Th. Langer proposes (German patent, No. 55544, Kl. 18, 1891) the following mixture:

Common salt	15 parts
Yellow prussiate of potassium	5 parts
Borax	1 part

or the other:

Common salt	3.2 parts
Yellow prussiate of potassium	0.3 part
Charred horn parings	0.5 part
Borax	0.07 part

As is seen, the inventor considers that the borax exercises its action even when used in quite small proportions.

The same remarks may be repeated for the following mixture proposed by Gallet (United States patent, No. 146330, 1874):

1.	Alumina, from	0.5 to 1 gram
2.	Highly aluminous clay	12 to 20 grams
3.	Pulverized wood charcoal and lamp black	50 grams
4.	Calcium carbonate	38 to 42 grams
5.	Potassium carbonate	18 to 30 grams
6.	Sodium carbonate	2 grams
7.	Caustic potash	0.5 to 1 gram
8.	Manganese oxide	4 grams
9.	"Rosin"	4 to 5 grams
10.	Common salt	1 gram
11.	Sal ammoniac	0.5 to 1 gram
12.	Borax	0.5 to 1 gram
13.	Water	about 10 per cent. of total weight

In this powder, which constitutes an interesting example of those complex mixtures referred to several times in the preceding chapter, not only the borax but even several of the other substances are present in homeopathic doses. Thus, the question naturally arises as to what specific efficacy half a gram of alumina can have along with 12 grams of clay, or 2 grams of sodium carbonate along with 18 or 30 grams of potassium carbonate.

Another mixture of the same kind is the following, proposed by F. G. Bates (German patent, No. 83093, Kl. 18, 1895):

Carbon	90 parts
Cryolite	10 parts
Manganese oxide	20 parts
Common salt	1 part
Saltpeter	1 part
Spent lime	10 parts
Alum	10 parts

That 1 gram of common salt must truly be of great importance in such a mixture!

Just as curious is the mixture patented by F. André (see English patent, No. 1356, 1906), composed of potassium ferrocyanide, hide clippings, wood charcoal, resin, soda, earth, saltpeter and graphite. And that patented by Cattaneo and Faggian (see English patent, No. 13931, 1906), containing scrapings of ox horns, prussiate of potash, Peruvian bark, potassium bichromate, common salt, saltpeter, tartaric acid, boric acid, sal ammoniac, sulphuric acid, resin or colophony, magnesia, sawdust, carbon and soot.

Then, there are not lacking inventors who indicate in detail the special virtues of each of the ingredients of their complex mixtures. Thus, John Buckland Jenkins (United States patent, No. 490660, 1898) says (p. 1, lines 37 47) that his "compound" is formed of the following "reagents:" "A carbonaceous substance, such as wood charcoal, which imparts hardness to the product; manganese dioxide, which produces malleability and ductility; sodium chloride, which softens and gives tenacity; potassium cyanide, which hardens and makes the steel take the temper better; and ammonium chloride, which serves the same purpose as the potassium cyanide but costs less and is therefore used in greater proportions, nitrogen being the essential element." The sureness and the precision with which Mr. John Buckland Jenkins has succeeded in distributing the various functions among the various constituents of his mixture must certainly arouse envy in every experimenter.

We could continue for many and many a page the list of patented cementation mixtures like those reported above, but having our doubts of the usefulness of completing such a list, we forbear.

We will cite only one other example, which confirms the fact that many of the descriptions filed with applications for patents are skilfully written in a purposely uncertain and inexact way, so as to make it impossible for any one reading them to apply the process. The French patent No. 327984 of June, 1902 (Lecarme), proposes to prepare the cementing mass by the combination, in varying proportions, of the two following mixtures:

(*A*)	Wood charcoal in fine powder..................	1 liter
	Concentrated aqueous solution of potassium cyanide	1 liter
(*B*)	Powdered carbon..............................	1 liter
	Saturated solution of potassium ferrocyanide......	1 liter

This mass is to be used either as a "varnish" (see p. 284) or, mixed with charcoal, to form the filling of the ordinary cementation boxes. Now, it is clear that a mixture containing such a large proportion of water could not be used in the usual cementation boxes without some special arrangement for permitting the easy escape of the great quantities of water vapor which would rapidly form in these boxes, nor without some means capable of preventing the harmful action which water vapor produces when evolved *in contact* with the surface of the pieces subjected to the treatment.

Various processes of cementation are based on the use of aqueous solutions of various carburizing substances.

These solutions are to be used by immersing in them the objects of steel at white heat; the objects are thus simultaneously cemented (as the result of the carburizing substances dissolved in the bath) and hardened by the sudden cooling produced by the immersion in the liquid. Among the patents of this group is the English patent No. 2981, 1890 (M. F. Coomes and A. W. Hyde), which recommends the use of aqueous solutions of sugar, molasses, oxalic acid and alkali oxalates, tartaric acid, etc. The efficacy of processes of this kind is very doubtful.

There are, next, many other patents claiming the use of *one* well-defined substance which, used alone or added to the simplest cements of well-known action, produces rapid cementations. Among these patents, which in general are more worthy of notice than those of the preceding group, there are some which are certainly of no real practical importance. But, notwithstanding the large number of such patents, and the very great practical importance which they would have if they really gave practical results such as claimed by their inventors, I do not find that any of them have found practical application to any considerable extent. Besides this, in the few cases in which I have had occasion to try the substances designated in the patents of this group, I have not been able to obtain results better than those which are obtained with the cements ordinarily employed in all works.

Among these an example is that of Lamargese (English patent No. 25986, 1903), which claims the use of silica added to the wood charcoal of resinous plants.

Some experimental tests made to control the results of this mixture did not give results appreciably different from those obtained with other solid cements.

To the same group belong the patents of the "Cyanid-Gesellschaft" (see, for example, the English patent No. 16412, 1904, and the French one, No. 345642), claiming the use of cyanamide or of its compounds with the alkali or alkaline earth metals as cements. According to these patents, the mixture of eighty parts by weight of calcium cyanamide with twelve parts of wood charcoal is especially to be recommended. Guillet, who has tried these substances, has been able to establish[1] that they furnish results inferior to those which are obtained with the mixture of carbon and barium carbonate.

Thus, also, I do not find that there are at present employed, or at least not on a large scale, the processes patented by Engels (see, for example, the French patent No. 337154, 1903), which consist in using as cementing substance carbon silicide mixed with materials (such as sodium sulphate) capable, according to Engels, of assisting its decomposition.

Besides the means based on the choice of the carburizing material, other expedients have been studied to render the cementation more rapid. As an example, that patented in 1895 by A. Ammermann Ackermann (see German patent No. 79429, Kl. 18), consisting in hollowing out on the surface of the metal to be cemented a large number of grooves, of a depth proportioned to the thickness of the pieces to be cemented, placed close to each other in such a way as to completely cover this surface. In this way the surface on which the process of the penetration of the carbon by diffusion takes place is greatly increased and the quantity of the carbon which penetrates into the steel in the unit of time, all other conditions being equal, is likewise increased. The cementation being finished, the pieces are subjected, while hot, to a mechanical treatment (forging, rolling, etc.), capable of restoring to their surface its original form by leveling the ridges between the various grooves. The method was proposed by Ackermann especially for the cementation of plates, for which the restoration of the plane surface could be easily obtained by simple rolling of the rough ("grooved") cemented surface.

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[1] *Génie Civil, loc. cit.*

This procedure presents two serious disadvantages: the first, which it was easy to foresee, consists in the practical difficulty of rolling the grooved and highly carburized surface until it is again wholly plane, without harm to the qualities of homogeneity, compactness and continuity which are required of the metal of the cemented zones. The second disadvantage is that the cementation does not take place uniformly at all points of the surface but gives rise to a much more intense carburization of the edges in relief, for which the relation between the external surface (on which the cementation takes place) and the volume of the metal carburized as the result of a definite depth of penetration of the carbon is greatest. These differences between the concentrations of the carbon in the various parts of the metallic piece may attain very high values, especially if the grooves hollowed out on the surface of the steel are deep and numerous, and they cannot be eliminated practically by means of succeeding heat treatments. The regions thus super-carburized become brittle as the result of the hardening.

Another expedient proposed several times (see, for example, the English patent, Cowden, No. 13761, 1904) to obtain more rapid cementations than those which can be obtained by the usual processes consists in making the cementation begin as soon as the metal begins to solidify. Thus, in the process protected by the English patent just referred to, the steel is cast in a mold which, besides containing an arrangement designed to effect the enrichment of the steel in manganese only in some parts of it, is supplied with cavities filled with masses of carbon, the surface of which forms definite portions of the mold itself. In this way, the ingot of steel, which is obtained by casting the fused soft metal in such a mold, absorbs carbon only in those parts of its surface where the mold is composed of carbon. Moreover, the carburization of the metal should take place quite rapidly, as the diffusion of the carbon would begin at the surface of a mass of steel in the state of only incipient solidification. I do not find that this process, which the inventor indicates as being especially adapted to the manufacture of toothed wheels, is applied at present, and I have cited it only as an example of the numerous expedients proposed either to accelerate or to localize the cementation.

One of the means by which inventors have often tried to obtain rapid cementation is the use of electrical energy.

In the majority of cases the electrical phenomena are utilized only for their heating effect; but in other cases the inventors also try to utilize an assumed specific action of the electric current, which is supposed to behave as a carrier capable of facilitating, independently of the heating effect, the diffusion of the carbon into the mass of the solid steel.

These attempts have already been spoken of briefly in the first part of this volume (see p. 28). Among the patents concerning processes of this kind I shall cite, as example, only the German patent No. 46200, Kl. 48, 1888, and the corresponding English one, No. 9782, 1887, to Robert Kirk Boyle, according to which the iron object to be cemented is connected electrically with the *negative pole* of a generator of current, and at a short distance from its surface, sprinkled with carbon dust, is placed a conductor connected with the *positive pole* of the generator, so that an electric arc may be formed between this conductor and the surface of the steel. To the same group belongs the patent of Georg Mars (German application No. 37948, Abt. VI).

Considerably more numerous are the patents claiming processes of cementation where the electric current is used exclusively as the means of heating. In the patents of this group are described innumerable arrangements, often very complicated, adapted to utilizing in the best way the thermal effects of the electric current. I shall cite only a few, as examples.

Thus, M. Ruthenberg (English patent, No. 19547, 1907) claims the use of a simple electrical resistance furnace, in which the resistor, formed of granular materials or of carbon rods, is separated from the carburizing mass, wood charcoal and barium carbonate.

In the processes described in other patents, such, for example, as those of C. Davis (English patents, Nos. 22233 and 25671, 1901) (in which reference is also made to the heating by means of the electric arc) and of the "Société Anonyme l'Industrie Verrière et ses dérivés" (English patent, No. 5094, 1904), the cementing mass itself acts as the resistor, capable of transforming the electrical energy into heat.

In other patents, finally, are claimed processes in which the resistant mass is composed of the steel objects subjected to the cementation. Among these are the American patent No. 443464 of the "America Spring Co. in Illinois," which is for a continuous process of cementation and of hardening of iron wire; the wire, while it slowly passes through the cementation powder and the hardening bath, is traversed by an electric current sufficient to keep it at the desired temperature.

Very numerous patents claim special types of cementation furnaces, and it would not be possible to give here a complete list of them. Some examples chosen from those based on principles differing markedly from the furnaces

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most frequently used in industry have been already described in the preceding chapters.

There are numerous patents concerned with bringing the producer gas, used as cement, directly from the producer to the cementation chamber.

One of the many furnaces of this kind is that protected by the English patent No. 12291, 1901 (Clinch Jones). In it the gas, made in an ordinary producer placed at the lower part of the furnace, issues through two channels, one of which leads a part of it to a combustion chamber, in which it is burnt by air led in through suitable openings, while the other channel leads the remainder of the gas produced into the cementation chamber, heated to the desired temperature by the combustion chamber mentioned above.

The use of ordinary producer gas as cement might, in theory, be justified by the fact that in it carbon monoxide and the hydrocarbons act simultaneously, and we have seen the many advantages which can be obtained by the rational use of these mixtures. But we have also seen that these advantages consist essentially in the possibility of varying at will the concentration and the distribution of the carbon in the cemented zones by means of an *exact* regulation of the ratio between the quantity of carbon monoxide and that of the hydrocarbons contained in the gaseous mixture. It is evident, therefore, that the direct use of ordinary producer gas, for which such an exact regulation is not practically possible, can not give the result mentioned above with the sureness and the precision necessary in practice.

Another problem which various inventors have set themselves, for the purpose of avoiding the very serious disadvantage of the slowness with which heat is propagated from the periphery to the center of the ordinary cementation boxes charged cold, is that of heating separately both the cement and the pieces to be cemented to the temperature of cementation before placing them in contact with each other.

We have already seen how this problem is solved in a very simple and sure way by the processes of cementation, protected by various patents of 1908 and the following years, of the Società Ansaldo & Co. of Genoa, based on the use of mixed cements with carbon and carbon monoxide as base.

For these cements the solution is particularly easy and practical owing to the fact that the solid part of these cements is constituted of the simple "granular" carbon, forming a very mobile mass, especially when hot, which it suffices to "pour" on the objects to be cemented to completely fill the deepest cavities of the most complicated form, and also owing to the fact that the mixed cement, acting preponderantly through the effect of its gaseous constituents, extends its action, with undiminished efficacy, even to the parts of the surface of the steel pieces which are not in immediate contact with the solid carburizing substances. With all the other solid cements, whose efficacy is dependent upon a good contact with all points of the surface of the object to be cemented, the solution of the problem is considerably less simple, for the operation of the "tamping" of the cement around the steel pieces can not be thought of when the pieces and the cement are heated to redness. And, in fact, we do not find that processes which permit of introducing the charges *completely* heated, employing the usual solid cements, are actually used on an industrial scale.

At any rate, we shall cite, simply as an example, one of the patents claiming a process of this kind; the French patent No. 421961 (October 28, 1910–January 7, 1911), of the "Société des Établissements Partiot." One of the arrangements proposed in this patent consists in using a retort with two arms, arranged at a right angle with respect to each other, both heated in a suitable furnace. In the first phase of the operation, one of the arms of the retort—that placed vertically—contains only the cement, while the other—placed horizontally—contains only the pieces to be cemented. When the cement and the pieces are heated to the temperature adapted to the cementation, the cement is made to pass from the vertical arm of the retort into the horizontal one in such a way as to fill the spaces left free by the steel pieces. The commencement of the cementation is taken as from this moment. In the text of the patent just referred to, it is justly pointed out that one of the chief advantages of cementations carried out by starting with charges completely heated, as compared with those carried out in boxes charged cold, consists in the possibility of computing with exactness the time during which the process of cementation is really effected; this permits of obtaining with precision the desired results.

We might speak here of patents concerning the processes of cementation designed for the manufacture of ship armor, but a discussion of these patents, limited to what is explicitly said in them, would have no interest, because in their specifications, even more than in other patents, the "rule" of giving the least possible exact information useful for the practical application of the processes is closely followed. It would therefore not be possible for me to treat of the "true" content of these patents.

Similar reasons arise from the fact that for some time I have been conducting fruitful experimental investigations in this field at the expense and for the use of others, and so are prevented from giving here an analytical examination of the "*real*" content of the very numerous patents claiming the socalled "metallic cementation," including under this any process which permits of producing the diffusion of elements other than carbon into solid steel.

The great practical importance of the processes of this group has certainly been seen by many of the inventors of cementation mixtures, for many of the patents which claim the invention of carburizing powders or pastes contain additions in which is pointed out how, by adding certain compounds of definite metals (in general, nickel, manganese, chromium, tungsten, etc.) to the carburizing mixtures protected by the patent, the diffusion of those metals into the solid steel can also be produced, together with the diffusion of the carbon.

We will cite some examples chosen from the many patents containing such an "appendix." One of these is the German patent No. 83093, Kl. 18, 1895 (Francis Gordon Bates), which claims the addition of manganese oxide and of nickel oxide to the carburizing mixture specified in a preceding patent of the same inventor (No. 57729) to produce the diffusion of the two metals into the steel. Another is the German patent, No. 79429, Kl. 18 (Ackermann), which I have already cited. Still another is the French patent No. 327984, 1902, of J. Lecarme, already cited, and from which I wish to take and report here the composition of one of the mixtures recommended to obtain a zone of chromium steel:

Fine carbon	200 grams
Water	1,000 grams
Dextrin	200 grams
Pulverized potassium ferrocyanide	100 grams
Potassium chromate	100 grams

Other patents also take into account the way in which the heating of the pieces during the cementation is to be carried out. Among these are two German patents, Nos. 211201 and 231971.

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